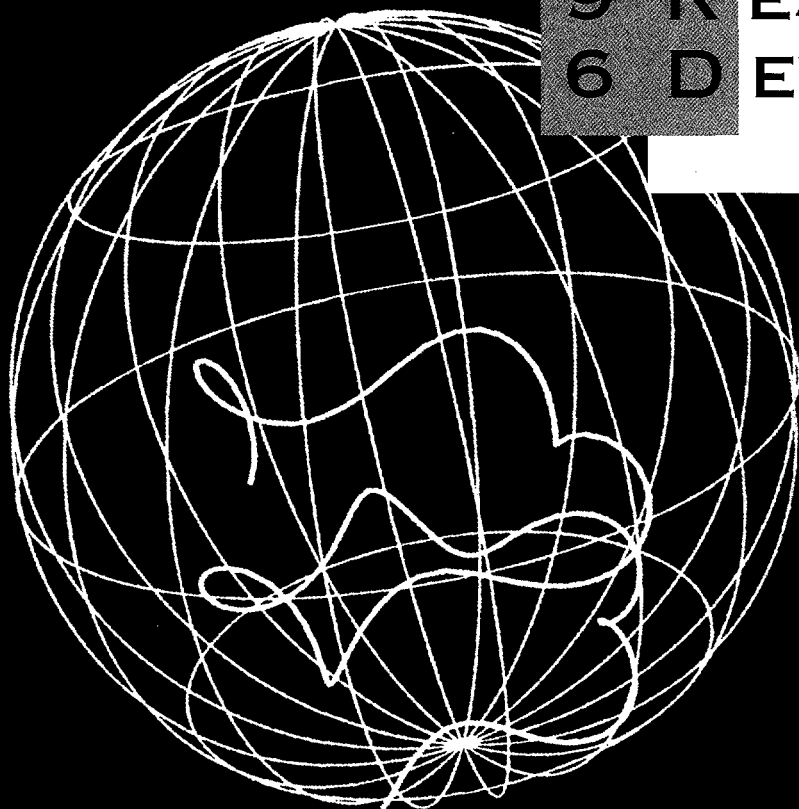


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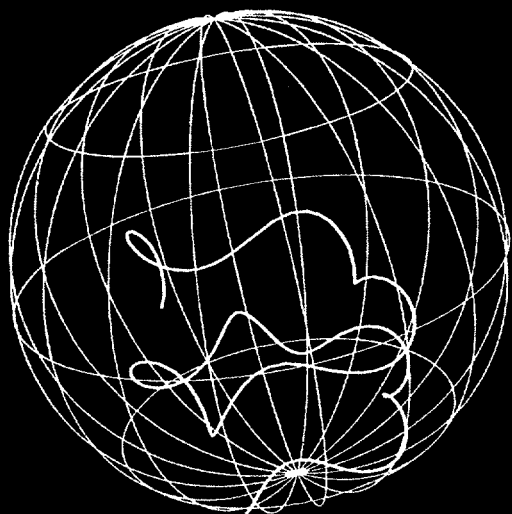
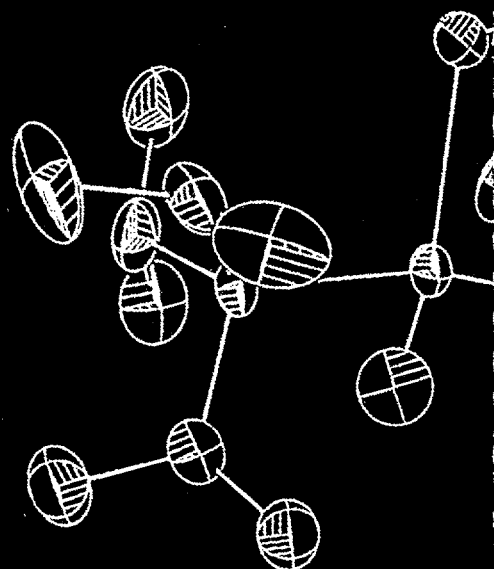
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ABSTRACT

This report summarizes the FY 1996 goals and accomplishments of Laboratory-Directed Research and Development (LDRD) projects. It gives an overview of the LDRD program, summarizes work done on individual research projects, and provides an index to the projects' principal investigators. Projects are grouped by their LDRD component: Individual Projects, Competency Development, and Program Development. Within each component, they are further divided into nine technical disciplines: (1) materials science, (2) engineering and base technologies, (3) plasmas, fluids, and particle beams, (4) chemistry, (5) mathematics and computational sciences, (6) atomic and molecular physics, (7) geoscience, space science, and astrophysics, (8) nuclear and particle physics, and (9) biosciences.



$$\frac{\partial}{\partial y} \psi \frac{\partial}{\partial x} \nabla^2 \psi - \frac{\partial}{\partial x} \psi \frac{\partial}{\partial y} \nabla^2 \psi = \nu \nabla^4 \psi$$

FRONT COVER

The background graphic is an atomic force microscope image of the slip bonds on a stressed iron-silicon-boron magnetic ribbon (M. Hawley, "Scanning Probe Microscopy Competency Development"). The superimposed upper-left image shows the trajectory of a single deuterium-tritium fusion alpha particle through a magnetized target plasma (R. Kirkpatrick, "Generation and Compression of a Target Plasma for Magnetized Target Fusion"). To the right are two scattered-light images showing the effect of a low-density plasma on a high-intensity laser probe (J. Cobble, "High-Intensity Matter Interaction Physics"). The equation describes the transport of vorticity in turbulent fluid flow in two-dimensional Cartesian space.

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LABORATORY-
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RESEARCH AND
DEVELOPMENT

FY 1996 PROGRESS REPORT

COMPILED BY
JOHN VIGIL AND JUDY PRONO

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Laboratory Director: **Sig Hecker**

Director for Science and Technology Base Programs: **Al Sattelberger**

Office Leader for Laboratory-Directed Research and Development: **Ed Heighway**

Scientific Editor: **John Vigil**

LDRD Office Team: **Shelly Cross, Jo McCarthy, and Leonard Salazar**

Managing Editor: **Judy Prono (CIC-I)**

Editors: **Deborah Bacon, Ileana Buican, Marty DeLanoy,
Anne Garnett, Jennifer Graham, Sheila Molony,
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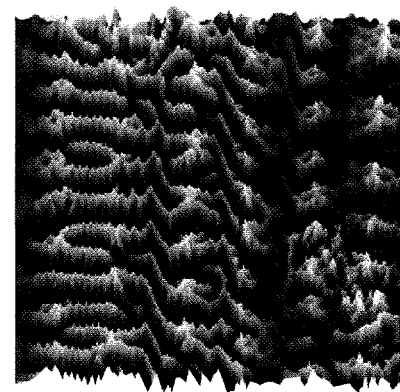
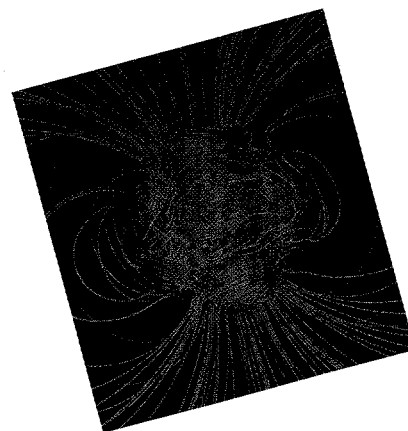
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Cover Design: **Susan Carlson (CIC-I)**

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Contents

1 LDRD Program Overview—FY 1996

Individual Projects

Materials Science

- | | | | |
|----|---|----|---|
| 9 | Origin of Radiation Damage in Potassium Titanyl Phosphate | 16 | Innovative Composites through Reinforcement Morphology Design—A Bone-Shaped Short-Fiber Composite |
| 10 | Development of a Fundamental Understanding of Chemical Bonding and Electronic Structure in Spinel Compounds | 18 | New Deposition Processes for the Growth of Oxide and Nitride Thin Films |
| 11 | Phase Stability of Transition Metals and Alloys | 18 | Texture Characterization for HE Design |
| 12 | Theoretical and Experimental Investigation on the Low-Temperature Properties of the NbCr ₂ Laves Phase | 19 | Interfacial Charge Transport in Organic Electronic Materials: The Key to a New Electronics Technology |
| 14 | Nanostructured Materials: Growth and Patterning Using Hyperthermal Materials Chemistry | 19 | Thermodynamic and Electrodynamical Studies of Unusual Narrow-Gap Semiconductors |
| 14 | Inorganic-Organic Composite Nanoengineered Films Using Self-Assembled Monolayers for Directed Zeolite Film Growth | 20 | A Molecular Architectural Approach to Novel Electrooptical Materials |
| 15 | Rigid Molecular Foams | 21 | Characterization and Manipulation of Broken-Symmetry Materials at Phase Boundaries |
| 15 | Materials Research for Optical Refrigeration | | |

Engineering and Base Technologies

- | | | | |
|----|---|----|--|
| 23 | Development of New and Efficient Hard-Rock Mining Methods Using Pulsed-Laser Excavation | 25 | The Development of Fullerene-Based Hydrogen Storage Systems |
| 23 | Virtual Reality and Telepresence Control of Robots Used in Hazardous Environments | 25 | Optical Imaging through Turbid Media Using a Degenerate, Four-Wave, Mixing Correlation Time Gate |
| 24 | Nuclear Magnetic Resonance Imaging with Hyperpolarized Noble Gases | 26 | High-Average-Power, Intense Ion Beam for Materials Modification and Other Applications |

Individual Projects (cont.)

Engineering and Base Technologies (cont.)

- | | | | |
|----|---|----|---|
| 27 | Multichip Module Technology Development | 32 | Application of Intense Surface Discharge VUV Light Sources to Photoresist Ashing in Semiconductor Manufacturing |
| 27 | Magnetic Resonance Force Microscope Development | 33 | All-Solid-State Four-Color Laser |
| 28 | Femtosecond Scanning Tunneling Microscope | 34 | Material Processing for Self-Assembling Machine Systems |
| 29 | Exploration of Technologies for Improving Civil Security | 34 | Diode Laser Development for Quantum Computation |
| 30 | Fiber-Optic Communications Using Solitons (FOCUS) | 35 | Designing a Micromechanical Transistor |
| 30 | New Applications for Zeeman Interferometry | 35 | High-Sensitivity, Solid-State Carbon Monoxide Sensor Development |
| 31 | A Comprehensive Monitoring System for Damage Identification and Location in Large Structural and Mechanical Systems | 35 | Acoustic Resonance Spectroscopy |
| 31 | Quantum Cryptography for Secure Communications to Low-Earth-Orbit Satellites | 36 | Liquid-Metal, Focused-Ion-Beam Etch Sensitization and Related Data Transmission Processes |
| | | 36 | Experimental Validation of Superconducting Quantum Interference Device Sensors |

Plasmas, Fluids, and Particle Beams

- | | | | |
|----|--|----|--|
| 37 | High-Power, High-Frequency, Annular-Beam Free-Electron Maser | 41 | Turbulence and Turbulence Spectra in Complex Fluid Flows |
| 38 | Determination of Optical Field-Ionization Dynamics in Plasmas through Direct Measurement of the Optical-Phase Change | 41 | A Water-Filled, Radio-Frequency Accelerating Cavity |
| 39 | Delta-f and Hydrodynamic Methods for Semiconductor Transport | 42 | A Target Plasma Experiment for Magnetized Target Fusion |
| 40 | A Compact Compton-Backscattering X-Ray Source for Mammography and Coronary Angiography | 43 | Developing Electron-Beam Bunching Technology at Subpicosecond Pulse Lengths for Improving Photon Sources |
| 40 | Equation of State of Dense Plasmas | 44 | High-Intensity Laser-Matter Interaction Physics |

Individual Projects (cont.)

Chemistry

- | | | | |
|----|--|----|--|
| 45 | New Fullerene-Based Mixed Materials: Synthesis and Characterization | 54 | Binding of Hydrocarbons and Other Extremely Weak Ligands to Transition-Metal Complexes that Coordinate Hydrogen: Investigation of <i>Cis</i> -Interactions and Delocalized Bonding Involving Sigma Bonds |
| 46 | Uses of Novel Selenium-Containing Chiral Derivatizing Agents: Potential Catalysis for the Chiral Oxidation of Simple Alkenes and Chiral-Promoted Aldol Reactions | 55 | Asymmetric Catalysis in Organic Synthesis |
| 47 | Metal-Ligand "Multiple" Bonding: Revelations in the Electronic Structure of Complexes of High-Valent f-Elements | 56 | Temperatures and Vibrational Frequencies of Liquid N ₂ /O ₂ and CO/O ₂ Mixtures Shock-Compressed to 10 GPa and 2000 K |
| 48 | Chemistry and Catalysis in Supercritical Media | 57 | Catalysts for Hydrocarbon Oxidation |
| 50 | Decay of Surface Nanostructures Via Long-Time-Scale Dynamics | 57 | Fundamental Studies of Polymer Filtration |
| 51 | Solvation and Ionic Transport in Polymer Electrolyte Membranes | 58 | Modification of Heterogeneous Chemistry by Realistic Substrate Complexity |
| 51 | Heterogenization of Homogeneous Catalysts: The Effect of the Support | 59 | Ionically Conducting Polymers for High-Energy-Density Batteries |
| 52 | Photoredox Reactions: Energy Storage and Halocarbon Degradation | 59 | Advanced Polymer Chemistry of Organometallic Anions |
| 52 | Reactivity at Metal Centers Bound to Water-Soluble Catalysts | 60 | Reaction Kinetics Relevant to the Recycle Hydride-Dehydride Process for Plutonium Recovery |
| 53 | Cyclodextrin-Based Chemical Microsensors for Volatile Organic Compounds (VOCs) | 60 | Ultrafast Laser Studies of Solution Reactivity |

Mathematics and Computational Sciences

- | | | | |
|----|---|----|---|
| 61 | Parallel Three-Dimensional Spherical-Harmonics Transport Methods | 63 | Dispersive Water Waves in One and Two Dimensions |
| 61 | Adaptive, Composite, Overlapping Mesh Algorithms on Message-Passing Architectures | 64 | Mimetic Difference Approximations of Partial Differential Equations |
| 62 | A Self-Consistent Multiscale Theory of Internal-Wave, Mean-Flow Interactions in the Ocean | 64 | Wavelet Transforms as Solutions of Partial Differential Equations |
| 62 | Geometry in the Large and Hyperbolic Chaos | 65 | Dispersive, Internal, Long-Wave Models |
| 63 | Industrial Processing of Complex Fluids: Formulation and Modeling | 65 | Solution-Adaptive Methods for Low-Speed and All-Speed Flows |

Individual Projects (cont.)

Mathematics and Computational Sciences (cont.)

- | | | | |
|----|--|----|---|
| 66 | Combinatorics, Geometry, and Mathematical Physics | 68 | Computational Three-Dimensional Inversion for Seismic Exploration |
| 66 | The Fundamental Role of Solitons in Nonlinear Partial Differential Equations | 68 | Super-Speed Computer Interfaces and Networks |
| 67 | Elliptic Solvers for Adaptive Mesh Refinement Grids | 69 | Particles and Patterns in Cellular Automata |
| 67 | Studies of Structure of Turbulence by High-Resolution Simulation and Theory | 69 | High-Quality Finite-Difference Schemes for Partial Differential Equations and Discrete Vector and Tensor Analysis |
| | | 70 | Modeling Mesoscopic Phenomena in Extended Dynamical Systems |

Atomic and Molecular Physics

- | | | | |
|----|---|----|--|
| 71 | State-to-State Photodetachment in the Two-Electron Hydrogen Ion | 73 | Optical Wave Packets (Optical Bullets): A New, Diffraction-Free Form of Light Travel |
| 71 | Transient Quantum Mechanical Processes | 74 | Nonlinear Atom Optics |
| 72 | Calculation of Satellite Line Structures in Highly Stripped Plasmas | 74 | Dynamics of Quantum Wave Packets |

Geoscience, Space Science, and Astrophysics

- | | | | |
|----|--|----|---|
| 75 | Low-Energy Neutral Atom Imager | 81 | Theoretical Research on Dwarf and Classical Novae |
| 76 | Nonlinear Processes in Earthquakes | 81 | Micro/Macroscale Coupling in Magnetospheric Plasmas |
| 78 | Lead Immobilization in Thermally Remediated Soils and Igneous Rocks | 82 | Numerical Simulations of Convection Experiments and Earth's Interior |
| 78 | Experimental Studies of Auroral-Arc Generators | 83 | High-Velocity Neutron Stars |
| 79 | Fundamentals of Laser Ablation in the Analysis of Geological Materials | 83 | Sedimentary Basin Response to Strong Motion in Populous Regions |
| 80 | Integrating Chemistry into Three-Dimensional Climate Models: Detailed Kinetics in the Troposphere and Stratosphere of a Global Climate Model | 84 | Heterogeneous Processing of Bromine Compounds by Atmospheric Aerosols: Relation to the Ozone Budget |
| 80 | Using Microspheres as Tracers for Flow in Geologic Media | | |

Individual Projects (cont.)

Geoscience, Space Science, and Astrophysics (cont.)

- | | | | |
|----|--|-----|--|
| 85 | Coronal Mass Ejections in the Solar Wind | 95 | Close Encounters of Asteroids and Comets to Planets |
| 85 | Modeling Core-Collapse Supernovae in Three Dimensions | 95 | Isotopic Prediction of Eruption Volume at Continental Volcanoes |
| 86 | Deriving the Structure of Presupernovae and Delta Scuti Stars Using Nonradial Oscillations | 96 | Experimental Cosmology: The Early Universe |
| 88 | Magmatic Tritium | 98 | Cosmology with Massive Neutrinos |
| 90 | Minerals of Earth's Deep Interior | 98 | Global Climate Effects of the Emerging Chinese Transportation System |
| 91 | Striation-Image Monitoring of Plasmaspheric, L-Resolved Electrodynamics (SIMPLE) | 99 | Regge Geometrodynamics in Support of Gravity Wave Astronomy |
| 91 | Coupled Ocean-Atmosphere Model System for Studies of Interannual-to-Decadal Climate Variability over the North Pacific Basin | 99 | Remote Sensing of Thundercloud Electric-Field Airglow |
| 92 | Particle Acceleration from Reconnection in the Geomagnetic Tail | 100 | Accretion onto Black Holes: The Power-Generating Mechanism |
| 93 | Fluxes of Water and Energy in Physically Heterogeneous Environments | 102 | Thermal Rocketing and the Laser Geodynamic Satellite (LAGEOS-1) |
| 94 | Flare Star Monitoring with a New Single-Photon-Counting Imaging Detector | 102 | Plasmasphere Refilling: New Numerical and Observational Tools |

Nuclear and Particle Physics

- | | | | |
|-----|--|-----|---|
| 103 | Time-Reversal Tests in Polarized Neutron Reactions | 109 | Antiquark Distributions in the Proton |
| 104 | Exploring and Testing the Standard Model and Beyond | 109 | Nucleon-Nucleon Data Analysis |
| 104 | L3 Physics at the Z Resonance and a Search for the Higgs Particle | 110 | Solar Neutrino Physics |
| 105 | Neutrinos and Theory of Weak Interactions | 111 | Chiral Symmetry in Finite Nuclei |
| 106 | Weak Interaction Measurements with Optically Trapped Radioactive Atoms | 111 | Simulating the Decays of Bottom and Charm Mesons |
| 108 | Neutrino Physics at Fermilab | 112 | Nonequilibrium Dynamics of the Quark-Gluon Plasma in Heavy-Ion Collisions |
| 108 | A Continuous Watch of the Northern Sky above 40 TeV with the CYGNUS Array | 113 | Determination and Study of Cosmic-Ray Composition above 100 TeV |
| 108 | Neutron Measurements to Optimize Treatment of Cancer Patients with Fast Neutrons | 114 | Nonperturbative Estimates of the Standard Model Parameters |

Individual Projects (cont.)

Biosciences

- | | | | |
|-----|--|-----|---|
| 115 | Biotechnology Approaches to Stable-Isotope Labeling for Biomolecular Structure/Function Studies | 121 | Engineering Sequence-Specific RNA and Single-Stranded-DNA Binding Proteins |
| 116 | Preparation and Utilization of ^{13}C - and ^{15}N -Labeled DNAs for the Determination of Unusual DNA Structures Relevant to the Human Genome Project by Nuclear Magnetic Resonance Spectroscopy | 122 | Theoretical Studies of Allosteric Changes and DNA Binding of a cAMP-Dependent Transcription Activation Protein |
| 116 | Applications of Strand-Specific In Situ Hybridization | 122 | Engineering the Specificity of xylR: A Bacterial Protein that Detects Chemicals in the Environment |
| 117 | Computer Simulation of Protein Solvation, Hydrophobic Mapping, and the Oxygen Effect in Radiation Biology | 123 | Optimization and Monitoring of Hollow-Fiber Bioreactors |
| 117 | Electromagnetic Inverse Applications for Functional Brain Imaging | 124 | Optimal Screening Designs for Biomedical Technology |
| 118 | Gene Shuffling Using Flow Cytometry | 126 | Nuclear Magnetic Resonance (NMR) Spectroscopy of Unusual DNA Structures and Functions Associated with Human Disease |
| 118 | Identification and Characterization of a Human DNA Double-Strand Break Repair Complex | 127 | Emerging Pathogens: Dynamics, Mutation, and Drug Resistance |
| 119 | Determining the Role of the Telomere on the Severity of Birth Defects | 127 | Optical Measurement of Drug Concentrations in Tissue |
| 119 | Development of an Ultrasensitive and Rapid DNA Repair Assay | 128 | Stable-Isotope Labeling of Oligosaccharide Cell-Surface Antigens for Structural Studies |
| 120 | Structure and Thermodynamics of Surface Recognition | 129 | Protein Motions that Determine the Efficiency of Photosynthesis |
| 120 | Neutron Structural Biology | 129 | Studying Properties of Cell Suspensions with Elastic Scattering |
| 121 | Sum-Frequency Generation Studies of Membrane Transport Phenomena | 130 | Numerical Simulations of Biochemical Self-Organization: Calcium Wave Propagation and Microtubule Growth |

Competency Development Projects

Materials Science

- | | |
|--|--|
| 135 Actinide Crystal Structures with an Emphasis on Plutonium Alloys | 148 Characterization of Active Sites in Zeolite Catalysts |
| 136 The Implications of Diffraction In Situ Loading Macrostrain Measurements in Composites and Finite-Element Interpretations | 149 New Initiatives in Materials Characterization, Modeling, and Synthesis |
| 137 Chemical and Physicochemical Properties of Submicron Aerosol Agglomerates | 149 Dynamics of Polymers at Interfaces |
| 137 Characterization of Bioactive Materials Using Neutron Reflectivity and Atomic Force Microscopy | 150 Understanding and Controlling Self-Assembly |
| 138 Bulk Amorphous Materials | 151 Role of Charge Localization in the Basic High-Temperature Superconductivity Mechanism |
| 139 Characterization of Advanced Electronic Materials | 152 Measurement by Neutron Diffraction of Strains in Advanced Engineering Structural Materials including AlSiC and AlTiC |
| 140 Neutron Scattering Studies on Shear-Induced Structure in Polymers | 153 Chemistry and Microstructure of High-Temperature Superconductor Interfaces |
| 140 Structural and Magnetic Characterization of Actinide Materials | 154 Texture Science and Technology |
| 142 Equation-of-State, Thermodynamic, and Structural-Mechanical Properties of Intermetallic Compounds | 154 Microstructures of Transition Metal Oxides Characterized by Neutron and X-Ray Scattering |
| 142 Neutron Scattering from Correlated-Electron Systems | 155 A Thermodynamically Consistent, Damage-Dependent, Interface Debonding Model for Composites |
| 143 Advanced Deformation Process Modeling | 155 Zircon as a Host Phase for Plutonium Disposition |
| 144 Scanning Probe Microscopy Competency Development | 156 Many-Body Theory Research |
| 145 Design and Implementation of an X-Ray Strain Measurement Capability Using a Rotating Anode Machine | 157 Alloy Design and Phase Stability of the Ternary Alloy Ti-Al-Nb |
| 146 Computational Modeling of Materials Processing and Processes | 158 Synthesis and Characterization of Correlated-Electron Materials |
| 146 Nanometer-Scale Materials | 159 Tailoring the Interfacial Electronic Structure of Organic Electronic Materials and Devices |
| 147 Science and Technology of Reduced-Dimensional Magnetic Materials | 159 Controlling Function of Polar Organic Multilayers |
| 147. Complementary Neutron Diffraction and Computational Micromechanics Studies of Polycrystalline Deformation in Advanced Materials | 160 Pinning Vortices and Enhancing High-Temperature Superconductor (HTS) Critical Currents |
| | 161 Nonlinearity in Structural and Electronic Materials |
| | 163 High-Resolution Electron Microscopy of Advanced Materials |

Competency Development Projects (cont.)

Engineering and Base Technologies

- | | | | |
|-----|---|-----|---|
| 167 | Molten Salt and Molten Lead Systems Studies | 172 | Development of Inexpensive Continuous-Emission Monitors for Feedback Control of Combustion Devices to Minimize Greenhouse Gases, Toxic Emissions, and Ozone-Damaging Products |
| 168 | Advanced Measurements and Techniques in High Magnetic Fields | | |
| 168 | Dynamic High-Strain Deformation of Materials: Experiments, Advanced Constitutive Modeling, and Computational Implementation | 173 | Distortion, Residual Stress, and Thermal Gradient Issues for Plutonium Gravity Casting in Ambient-Temperature Molds |
| 169 | Ultrasensitive Sensors for Weak Electromagnetic Fields Using HTS SQUIDs for Biomagnetism, NDE, and Corrosion Currents | 174 | Radiation Resistance Measurements of Rare-Earth Permanent Magnet Material for High-Intensity Linac Applications |
| 170 | Short-Pulsed Electric-Discharge Degradation of Toxic and Sludge Wastes | 174 | Molten Salt and Separations Technologies Evaluation |
| 171 | Laser-Sheet Imaging of HE-Driven Interfaces | 175 | Neutron Metrology for Stockpile Stewardship at LANSCE |
| 171 | A Neural-Network-Based System for Damage Identification and Location in Structural and Mechanical Systems | | |

Plasmas, Fluids, and Particle Beams

- | | | | |
|-----|---|-----|--|
| 177 | High-Energy Test of Proton Radiography Concepts | 179 | Development of Ion-Beam Techniques for the Study of Special-Nuclear-Materials-Related Problems |
| 177 | Comparison of Cyclotrons and Linacs for High-Intensity-Beam Applications | | |
| 178 | A 1-kW-Power Demonstration from the Advanced Free-Electron Laser | 180 | Generation and Compression of a Target Plasma for Magnetized Target Fusion |
| 179 | Advanced Techniques for Producing, Polarizing, and Storing Ultracold Neutrons | 182 | Advanced Modeling of High-Intensity Accelerators |

Chemistry

- | | | | |
|-----|--|-----|--|
| 183 | Binding Carbon Dioxide in Mineral Form: A Critical Step toward a Zero-Emission Coal Power Plant | 185 | Kinetic Studies of Competitive Adsorption Processes Related to Automobile Catalytic Converters |
| 183 | Foreign Nuclear Test Radiochemical Diagnostics | | |
| 184 | The Characterization of Atmospheric Aerosols: Applications to Heterogeneous Gas-Particle Reactions | 185 | Investigations of Biomimetic Light-Energy-Harvesting Pigments |

Competency Development Projects (cont.)

Mathematics and Computational Sciences

- | | |
|---|---|
| 187 Nuclear Futures Analysis and Scenario Building | 195 Theoretical Foundation for Adaptive Monte Carlo |
| 188 New Numerical Models for Global Ocean Modeling | 196 Advanced Three-Dimensional Eulerian Hydrodynamic Algorithm Development |
| 188 Lie Group Applications to the Solution of Differential Equations | 198 Phase Transitions, Nonequilibrium Dynamics, and Critical Behavior of Strongly Interacting Systems |
| 189 Lithospheric Processes | 198 Numerical Simulations of Disordered Superconductors |
| 189 Geometrically Compatible 3-D Monte Carlo and Discrete-Ordinates Methods | 199 Transactional Memories: A New Abstraction for Parallel Programming |
| 190 Adaptive Monte Carlo Methods for Radiation Transport | 199 Development of an Integrated System for Estimating Human Error Probabilities and Modeling Their Effects |
| 191 High-Performance Computing of Electron Microstructures | 200 Novel Monte Carlo Algorithms for Statistical Mechanics |
| 192 Modeling Complex Phenomena: Multiple Length and Time Scales in Extended Dynamical Systems | 200 Advanced Computational Science |
| 192 Continuing Benchmarking of Ocean-Circulation Models | 201 Development of an Automated Core Model for Nuclear Reactors |
| 193 Simulation Methods for Advanced Scientific Computing | 201 Density Function Estimation for Monte Carlo Simulations |
| 193 Adaptive Mesh Refinement Algorithm Development and Dissemination | 202 Self-Organization and Pattern Formation |
| 194 Neutron Transport Methods for 3-D Cartesian Adaptive Meshes | 203 Application of Discrete Mathematics |
| 194 Applications of Nonlinear and Stochastic Dynamics | 204 Theory and Modeling of Correlated-Electron Materials |

Geoscience, Space Science, and Astrophysics

- | | |
|---|---|
| 207 Modeling the Heat Flow and Resulting Dynamics in Earth's Interior | 210 Analysis and Visualization of Global Magnetospheric Processes |
| 208 Remote Sensing Science Thrust: New Concepts | 211 Neutron Star Evolution and Emission |
| 209 Subsurface Noble Gas Transport at the Nevada Test Site | 212 Remote Sensing Science Thrust: Laser Remote Sensing |

Competency Development Projects (cont.)

Geoscience, Space Science, and Astrophysics (cont.)

- | | | | |
|-----|--|-----|---|
| 213 | Development of the First Nonhydrostatic, Nested-Grid, Grid-Point Global Atmospheric Modeling System on Parallel Machines | 216 | Studies of Dynamical Processes Affecting Global Climate |
| 213 | Production and Application of High-Specific-Activity Si-32 | 218 | Transport Processes in Space Plasmas |
| 214 | Remote Sensing Science Thrust: Hyperspectral Sensing | 220 | Physical Properties and Mantle Dynamics |

Nuclear and Particle Physics

- 223 Advanced Research Capabilities for Neutron Science and Technology—Neutron Polarizers

Biosciences

- | | | | |
|-----|---|-----|--|
| 225 | Solution Structure of the cAMP-Dependent Protein Kinase | 230 | Microbial Acquisition of Iron from Iron-Bearing Minerals |
| 225 | Development of Biosensors and Bioprobes Based on Spectroscopic Monitoring of Enzymes and Other Proteins Encapsulated in Sol-Gel Glasses | 230 | The Biology of Novel Animal Genes: Mouse APEX Gene Knockout |
| 226 | Molecular Characterization of Flow-Sorted Mammalian Centromeres | 231 | Competency Development in Antibody Production for Cancer Cell Biology |
| 226 | Advanced Biomolecular Materials Based on Membrane-Protein/Polymer Complexation | 232 | Covariation of Mutations: A Computational Approach for Determination of Function and Structure from Sequence |
| 227 | Similarity Landscapes: An Improved Method for Scientific Visualization of Information from Protein and DNA Database Searches | 233 | Structure, Dynamics, and Function of Biomolecules |
| 227 | Formation of Drug-Bearing Vesicles in Mixed Colloids of Bile Salts and Phosphatidylcholine | 234 | Advanced NMR Technology for Bioscience and Biotechnology |
| 228 | Structural Biology of Disease-Associated DNA Repeats and Protein-DNA Complexes Involved in the Repair of DNA Damage | 234 | Nonlinear Analysis of Biological Sequences |
| 229 | Applications of Optical Trapping to Single-Molecule DNA Sequencing | 235 | Indigenous Bacteria as Hosts for Proteins for Bioremediation |
| | | 236 | Landscapes and Dynamics of Proteins |
| | | 237 | Engineering Haloalkane Dehalogenase for Bioremediation |

Program Development Projects

Materials Science

- | | | | |
|-----|--|-----|---|
| 241 | Fundamental and Applied Studies of Helium Ingrowth in Plutonium | 243 | Giant Magnetoresistance Materials for Magnetic Recording Technology |
| 241 | Cost-Effective Development of Thin Films for Flat-Panel Displays | 243 | Characterizing Mechanical Effects of Aging Damage |
| 242 | Development of High Magnetic Fields for Energy Research | 244 | High-Magnetic-Field Research Collaborations |
| 242 | Advancing the Technology Base for High-Temperature Membranes | 244 | Ceramic/Polymer, Functionally Graded Material (FGM), Lightweight Armor System |
| | | 245 | New Anion-Exchange Polymers for Improved Separations in Nuclear and Industrial Applications |

Engineering and Base Technologies

- | | | | |
|-----|--|-----|--|
| 247 | Detection of Underground Structures and Tunnels | 251 | Modeling and Assessment of Concrete and the Energy Infrastructure |
| 247 | Active Noise and Vibration Control for Vehicular Applications | 251 | Global Nuclear Material Monitoring |
| 248 | Study of Possible Detector Geometries for Detection of Radioactivity in Moving Vehicles | 252 | Frequency-Resolved Optical Gating: A Diagnostic for the Characterization of Optoelectronic Materials and Devices |
| 248 | Environmentally Conscious Coal Combustion: Development of Process Monitors and Improved Numerical Models | 253 | Neutron-Based, Land-Mine Detection System Development |
| 249 | Establishing the Operational Durability of Polymer Light-Emitting Diodes | 254 | Development of the Transient-Reactor Analysis Code (TRAC) for Real-Time Applications |
| 249 | Helium-3 Targets for Tritium Production in Fission Systems | 254 | Rapid Prototyping of Hazardous Materials Using the Directed-Light Fabrication Process |
| 250 | Explosives Detector Using the Optical Signature of Deflagrating Explosive Particulates | 255 | Reactor-Based Tritium Production |
| 250 | Directed-Light Fabrication—A Laser Metal-Deposition Process for Fabrication of Near-Net-Shape Components | 255 | Methods for the Rapid On-Line Detection of Biological and Chemical Weapons |
| | | 256 | Night-Vision Device Technology Development |
| | | 256 | Integrated Approach to Advanced Machining |

Program Development Projects (cont.)

Plasmas, Fluids, and Particle Beams

- | | | | |
|-----|--|-----|---|
| 259 | Subsurface, Directed-Energy Methods for Groundwater Treatment | 261 | Advanced Ignition of Jet Turbine Engines |
| 260 | Plasma Source Ion Implantation for Advanced Manufacturing | 262 | Removal of Transuranic Materials from Contaminated Equipment Using Plasma Decontamination |
| 260 | Magnet Design Concepts for the 100-MeV Isotope-Production Facility | 262 | Supporting Technologies for a Long-Pulse Spallation Source |

Chemistry

- | | | | |
|-----|---|-----|---|
| 265 | Advanced Oxidation Technologies for Chemical Demilitarization | 268 | Integration of Advanced, Nuclear Materials Separations Processes |
| 266 | Advanced Nuclear Fuel Processing | 269 | Catalysis for Alternative Feedstocks |
| 267 | Chemical-Biological Treatment of Heterogeneous Wastes | 270 | Separation Science and Technology: Membrane-Based Separations and Destruction Processes |
| 267 | Radionuclide Separations Using Pillared Layered Materials | 271 | Microwave Processing Improvements for Methane Conversion to Ethylene |

Mathematics and Computational Science

- | | | | |
|-----|---|-----|---|
| 273 | Data Resources and Sample Applications for Information Analysis in Chemical and Biological Warfare Defense | 275 | Low-Speed Flow Hydrodynamics |
| 273 | Information-Handling/Data-Fusion Technologies to Extract and Analyze Export Information | 276 | A New Model to Estimate Regional Emissions Inventories |
| 274 | Intelligent Controllers for Battlefield Simulations | 278 | Improving Industrial Performance through Integrated Process Simulation, Control, and Optimization: Modeling Atoms to Enterprise |
| 274 | Visualization Capability for Nonproliferation and Emergency Training: A "Poor Man's" Virtual-Reality System | 278 | National Environmental/Economic Infrastructure System Model |
| 275 | Modeling for Environmentally Conscious Manufacturing | 279 | Global Nuclear Material Flow Model |

Atomic and Molecular Physics

- | | |
|-----|--|
| 281 | Measurement Criteria Analysis for Krypton, Xenon, and Hydrogen (Hydrogen/Deuterium/Tritium) Isotopes and Concentration Variability at Distance |
|-----|--|

Program Development Projects (cont.)

Geoscience, Space Science, and Astrophysics

- | | | | |
|-----|---|-----|--|
| 283 | The Carpinteria Reservoir Redevelopment Project | 285 | Improved Atmospheric Transport for Risk Assessment in Complex Terrain |
| 284 | Satellite-Based Laser Windsounder | | |
| 284 | Conditioning Geological Reservoir Realizations with Time-Dependent Data | 285 | Reservoir Enhancement on the Impermeable Margins of Productive Geothermal Fields: Integrated Resource Development and Management |

Nuclear and Particle Physics

- | | | | |
|-----|---|-----|---|
| 287 | Disposition of Plutonium as Nonfertile Fuel for Water Reactors | 288 | Measurement of Fissile Material in Spent Fuel and Alternate Nuclear Materials |
| 288 | An Ultracold Neutron Facility at the Manual Lujan Jr. Neutron Scattering Center | | |

Biosciences

- | | | | |
|-----|---|-----|--|
| 289 | A Consortium for Biomedical Applications of Single-Molecule Detection | 293 | Distributed Telemedicine for the National Information Infrastructure Testbed |
| 290 | Cancer Risk Assessment | 293 | Deformable Human Body Model Development |
| 290 | Human Brain Mapping: Experimental and Computational Approaches | 294 | Detection and Characterization of Biological-Weapons Agents by Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry |
| 291 | Universal Biological-Agent Point-Sensor Program Development | 294 | Novel Gene Complex Structure Determination by Neutron and X-Ray Scattering |
| 291 | Sensors for Point Detection of Chemical and Biological Warfare Agents | 295 | In Situ Bioremediation of Trichloroethylene-Contaminated Groundwater |
| 292 | Molecular Medicine for the 21st Century: A Computational Basis for Design and Critique of Vaccines and Therapeutics | | |

299 Index of Principal Investigators

Overview

LDRD Program Overview—FY 1996

Ed Heighway and John Vigil

The Laboratory-Directed Research and Development (LDRD) Program is authorized by Congress to fund internally proposed research and development that extends the Laboratory's science and technology capabilities in support of its mission. There are three ways in which LDRD helps extend these capabilities. First, the research explores new ways of tackling mission problems, thereby identifying opportunities to execute the Laboratory's mission in a cheaper, faster, or better way. Second, the research invests in new core capabilities needed to fulfill the mission, perhaps adding a multidisciplinary approach that provides new insight. And third, but by no means least, LDRD invests in the fundamental science and technology base that underpins the Laboratory's ability to execute its mission.

All three types of research are represented in the Los Alamos LDRD program. Projects are chosen based on their innovation and scientific merit in a mission context, and as a result the work leads to a large number of publications, patents, and external awards. These in turn result in greater visibility for the Laboratory's science and technology, and LDRD becomes a vehicle for attracting the best scientists and engineers.

The primary mission of Los Alamos National Laboratory is "to reduce the nuclear danger," and there are four major pieces of that mission: ensuring that the nation's nuclear stockpile is reliable and safe, managing the production and use of nuclear materials, ensuring that the environment is both restored from past nuclear activities and is minimally impacted by future activities, and

developing technology to help eliminate proliferation of nuclear materials and weapons. To show how these activities are supported at Los Alamos, a breakdown of the Laboratory's FY 1996 funding by major programs is shown in Fig. 1.

Program Structure

LDRD is a formally managed program that imposes accountability in the processes of selecting, conducting, and documenting projects. All projects are selected competitively through review by peers or scientific managers. Innovation and scientific excellence are key selection criteria. All projects must be in science and technology areas that support the Laboratory's mission.

The LDRD program at Los Alamos has three components—Individual Projects (IP), Competency Development (CD), and Program Development (PD)—each with slightly differing goals. The IP component is intended to fund the most far-reaching

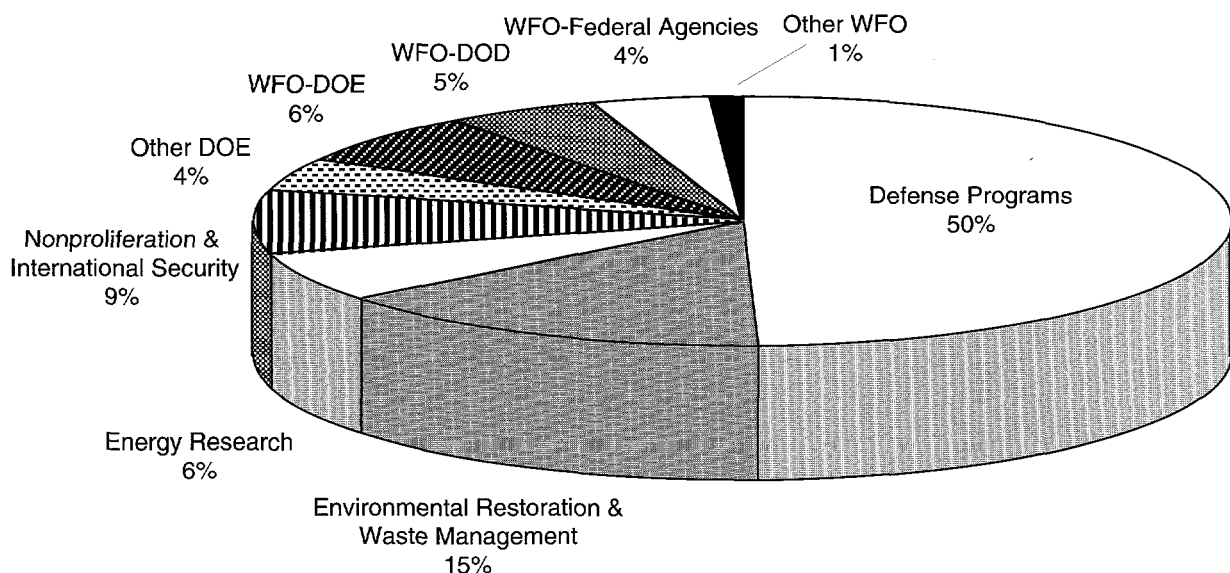


Fig. 1. Funding for major programs at Los Alamos National Laboratory during FY 1996.

and fundamental research proposed by technical staff members to extend the Laboratory's core science and technology base. The CD component invests in large multidisciplinary activities that tackle significant problems from several approaches, often combining theory and experiment. The PD component is intended to invest in nearer-term research for a specific sponsor that requires some exploration of feasibility or other confidence-building demonstration. In FY 1996, the LDRD program funded 356 projects at a total expenditure of \$54.9 million. The funding distribution among the three components is shown in Fig. 2.

Individual Projects. This component funds basic research whose potential is high but whose payoff may be distant. Often mapping uncharted territory, these projects are more exploratory than those of the other two components. Proposals are evaluated and ranked by peer-review teams (one team for each of nine technical disciplines), and the most highly ranked and relevant ones are

selected for funding. These projects are generally funded for three years. In FY 1996, 166 projects were funded.

Competency Development. This component funds the key science and technology competencies that support the Laboratory's missions and enable it to respond to new Department of Energy (DOE) and national issues. CD projects are intended to be cross-cutting: that is, they draw on the resources of several Laboratory divisions and have clear institutional value beyond the strategic interest of any single division. CD projects are proposed by the scientific staff through their technical division and program offices, are reviewed both for technical content and strategic value, and are ultimately selected by the Laboratory Director. In FY 1996, 117 CD projects were funded.

Program Development. This component funds research that allows the Laboratory to examine novel ways of meeting extended or future needs of program sponsors. Generally exploratory or demonstrational, this research assesses the feasibility of new scientific approaches or technologies and

establishes a technical path to advanced solutions of existing problems. PD projects are generally of shorter duration than those in the other two components, typically being funded for only one or two years. Proposals are solicited, reviewed, and selected by scientific managers and technical staff within the Laboratory's eight program offices. In FY 1996, 73 PD projects were funded.

The high quality of science supported by all three LDRD components is attested by the number of related scientific publications, patents, and awards. In 1996, LDRD projects generated 27% of all Laboratory publications, 39% of its patent awards, and half of the Laboratory's R&D 100 Awards—with only 5.5% of the budget. In addition, the LDRD program is a significant testing ground for the talent attracted to the Laboratory through its postdoctoral program. In 1996, 150 postdoctoral staff members worked on LDRD projects. Of these, many will go on to become permanent Laboratory employees and contribute to core scientific missions.

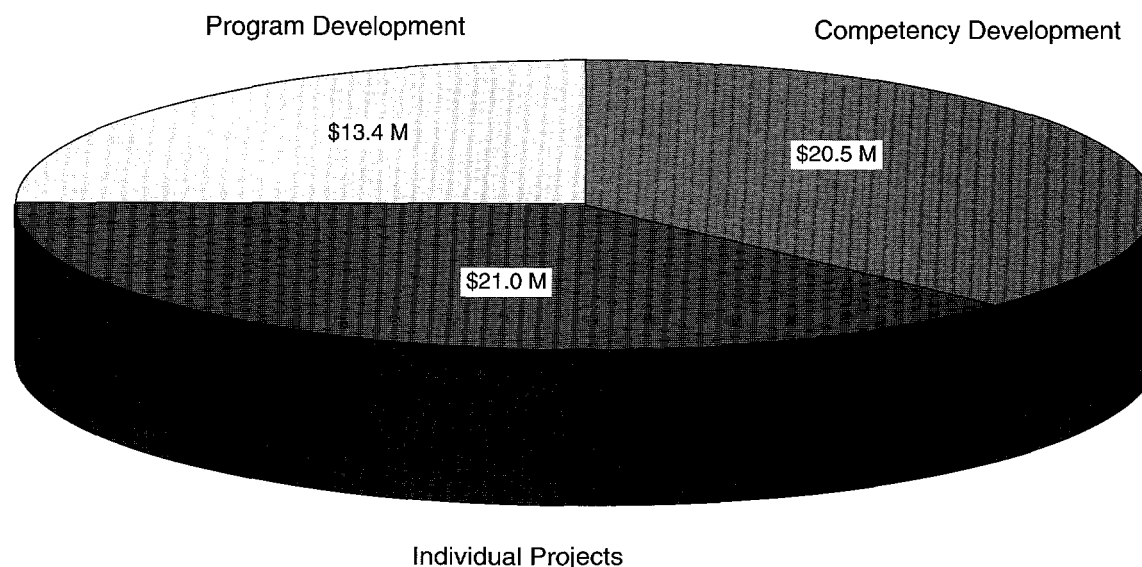


Fig. 2. Distribution of FY 1996 LDRD funding among the three program components.

Highlights of LDRD Support of National Security

LDRD projects tend to be cutting-edge research and contribute broadly to the science and technology base that supports the Laboratory's mission. They contribute to nuclear weapons science and technology, to nonproliferation, counterproliferation, and arms control, and to nuclear materials characterization and defense waste disposal, as well as to other national security areas such as materials, detectors, and computational tools for military applications. In this year's summary, we have chosen to highlight just a few LDRD contributions related to national security.

Nuclear Weapons Science and Technology. Without nuclear testing, a fundamental understanding of nuclear weapons performance becomes paramount. LDRD researchers are developing new ways to make the measurements needed for stockpile certification and for improving the modeling capability of nuclear weapons codes.

Recently, LDRD researchers identified a promising new approach for using high-energy protons to make high-resolution radiographs of very rapid events in high-density materials. Proton radiography's advantages are high spatial resolution, sensitivity to density variations, and the ability to capture the time history of an implosion. The LDRD program funded a proof-of-principle test that produced proton radiographs of a dense, *static* test object. Researchers are now developing the capability to make *dynamic* radiographs of dense objects under explosive compression.

The tendency of adjacent but dissimilar liquid layers to mix (interface instability) is a problem of central importance to nuclear weapons performance and simulation. In particular, the interfacial instability of a thin fluid layer driven by shock compression is a fundamental issue in turbulent mixing in nuclear weapons. LDRD researchers are developing a new measurement technique to obtain

"snapshots" of the evolving instability, leading to more accurate simulation models and improved calculations.

Understanding the effects of aging on nuclear weapon components, particularly plutonium and polymers, is an important aspect of science-based stockpile stewardship. LDRD researchers are making major contributions to this understanding through theoretical, computational, and experimental analyses. Using transmission electron microscopy, small-angle neutron scattering, and other advanced techniques, LDRD researchers are investigating alpha-decay-generated helium bubbles that form in aged plutonium metal. They are also developing computer simulation tools to evaluate the effects of this and other aging phenomena on properties that are germane to nuclear weapons safety and performance.

Degradation of polymers as they age is probably the most important factor limiting the lifetimes of stockpiled weapons. LDRD researchers are using both experiment and theory to link the large span of scales needed to accurately predict how changes in chemical structure, physical structure, and stress affect the mechanical properties of materials. Although aspects of each of the size scales (atomic, molecular, micro-, meso-, and macroscales) have been studied in the past, this LDRD work is one of the first attempts to link such a wide range of scales into a coherent picture that can be used to understand the behavior of polymeric elastomers.

Advanced Manufacturing Processes for the Weapons Program.

LDRD researchers have developed a new fabrication process called directed-light fabrication (DLF), and they are exploring its application to nuclear weapons fabrication (beryllium, uranium, and plutonium components). DLF is an automated, rapid, one-step method of making complex metal parts by fusing metal powder in the focal zone of a laser beam. The resulting parts are fully dense, have excellent structural

properties, and are shaped to within a few thousandths of an inch of final tolerance without the use of a mold, pattern, or forming die. The process is ideal for low-volume production of precision parts for both defense and civilian applications.

LDRD researchers have also developed and benchmarked computer simulations that predict distortion, residual stress, and thermal management in cast plutonium parts. Advances in these areas will benefit two DOE initiatives—Advanced Design and Production Technology (ADaPT) and the Accelerated Strategic Computing Initiative (ASCI).

Advanced Computational Capability and Nuclear Weapons Simulation. In the absence of nuclear testing, the ability to predict the performance of nuclear weapons based on computer simulations is one of the key requirements for maintaining a safe, secure, and reliable stockpile. Computer simulations of the complex phenomena that occur in a nuclear explosion continue to tax available state-of-the-art capabilities.

Past LDRD work has produced the discrete ordinates method for radiation transport, the particle-in-cell method for hydrodynamics, and other computational tools that are now used widely in both military and civilian applications. Today, LDRD researchers are providing the technology to implement these tools on the new generation of massively parallel supercomputers. They are also extending the capability of these tools through such developments as a complex geometric representation common to both Monte Carlo and discrete ordinate codes.

Computer simulations of nuclear weapons require not only the most powerful computers available, but also the ability to transfer huge amounts of computational data and display the data in forms that can be easily digested and analyzed. LDRD researchers have advanced the state of the art in fast data-transfer networks by inventing the high-performance

parallel interface (HIPPI), which supports local networks at data-transfer rates of 800 megabits/s (equivalent to transmitting one hundred 250-page books per second). Adopted as a standard by the American National Standards Institute, HIPPI has been implemented by many vendors and is currently the high-speed interface of choice for supercomputers. Building on this LDRD work, researchers have developed a synchronous optical network (SONET) gateway that can link supercomputers at HIPPI speeds over very large distances. Work is now under way to extend the network bandwidth to the 5 to 10 gigabits/s range.

Nonproliferation, Counter-proliferation, and Arms Control.

LDRD researchers are advancing the technology required to verify and monitor arms control treaties and to detect clandestine production of nuclear, chemical, or biological weapons.

Earth-orbiting satellites have detected transionospheric pulse pairs that are similar to the signature of a nuclear explosion. LDRD researchers have shown that these pulses can be explained by a runaway electron mechanism near thunderstorms that causes upward-propagating discharges called "sprites." Their new theory agrees with measurements of radio-frequency "chirp" pairs, as well as with optical and x-ray emissions associated with this phenomenon. This understanding will allow scientists to more accurately identify signals from clandestine nuclear explosions.

LDRD researchers are developing technology for detecting (with surrogates) chemical and biological warfare agents. The detection technology is based on the combination of membrane introduction and ion-trap mass spectrometry, and preliminary methods for continuous surrogate detection have been successfully developed. The surrogates include chlorobenzene, cyclohexanol, dimethyl methyl phosphonate, and

dimethyl sulfoxide and have been detected at approximately 100 ppb by volume in air.

Global proliferation of weapons-grade plutonium and highly enriched uranium has become one of the foremost threats to the security of the United States and the entire world. LDRD researchers are characterizing and modeling, from a global perspective, the management, control, and flow of weapons-grade nuclear materials. The objective of this research is to provide a computer-based tool capable of (1) capturing and enumerating data concerning the global inventory of nuclear weapons materials, (2) providing a global view of the management and control of nuclear materials, (3) undertaking macrosystem simulations of safeguards accounting surety and resource estimation, and (4) visually representing the nuclear materials information, including both inter- and intracountry flows.

Nuclear Materials. LDRD-funded activities at Los Alamos have contributed significantly to advanced methods for processing and recovering plutonium, to recovery of actinides and toxic metals from a variety of process streams, and to development of sensors for monitoring special nuclear materials.

LDRD researchers are exploring actinide crystal chemistry to learn why the ideosyncratic structures of plutonium metal occur. They are doing this by examining the crystal structures of several actinide alloys: neptunium-uranium, plutonium-thorium, and plutonium-zirconium. Such additional structural data may very well lead to a solution of the plutonium structure problem.

LDRD researchers are performing a series of laboratory-scale experiments to enhance the operation and safety of a new process for recovering metallic plutonium from nuclear

weapons. The hydride-dehydride recycle process eliminates the environmental hazards associated with other plutonium recovery methods. It takes advantage of plutonium's strong affinity for hydrogen gas. In the hydriding step, hydrogen reacts with the plutonium to form plutonium hydride powder, which is collected and then reheated to release the hydrogen (the dehydriding reaction), forming a metal powder. This metal powder is then melted to form storage-ready ingots.

LDRD researchers have developed and evaluated water-soluble chelating polymers for recovering actinide and toxic metals from a variety of process streams, as well as polymer filtration for recovering precious metals from industrial process streams. The high cost associated with the long-term storage of radioactive and toxic wastes mandates separating these components in a process waste stream before the waste is packaged and stored. A portable polymer filtration system that recovers zinc and nickel ions from electroplating rinse waters won an R&D 100 Award in 1995. LDRD researchers are now investigating membrane-based separation technologies for removing plutonium and americium from nuclear-materials-processing waste water, fission-product separations using cobalt dicarbide for solvent extraction, hollow-fiber membrane modules for separating gases and nuclear materials, and selective waste remediation using in situ photocatalytic reactors.

Other National Security Research.

LDRD contributions to other national security research include development of materials, detectors, and computational tools for conventional military applications, as well as sensors for environmental monitoring.

Intelligent computer-generated forces are an area of growing modeling importance within the Department of Defense (DoD). LDRD researchers are successfully using intelligent control and adaptive systems technology as well as advanced simulation software to develop, test, and demonstrate new intelligent actor capability in warfare simulations.

Resonant ultrasound spectroscopy (RUS) was originally used as a diagnostic tool in an LDRD project that studied the properties of high-temperature superconducting crystals. It was quickly determined that RUS could be used for nondestructively testing crystals for structural imper-

fections. The technique was further applied to detect cracks and other flaws in commercial and military hardware. RUS is now being used for nondestructively testing military components (aircraft landing assemblies, turbine disks, helicopter rotor parts, and ball bearings) and for identifying the contents of chemical munitions. Exploratory work is under way for using RUS to study the effects of aging on hemispherically shaped explosive charges as part of the Laboratory's stockpile stewardship mission.

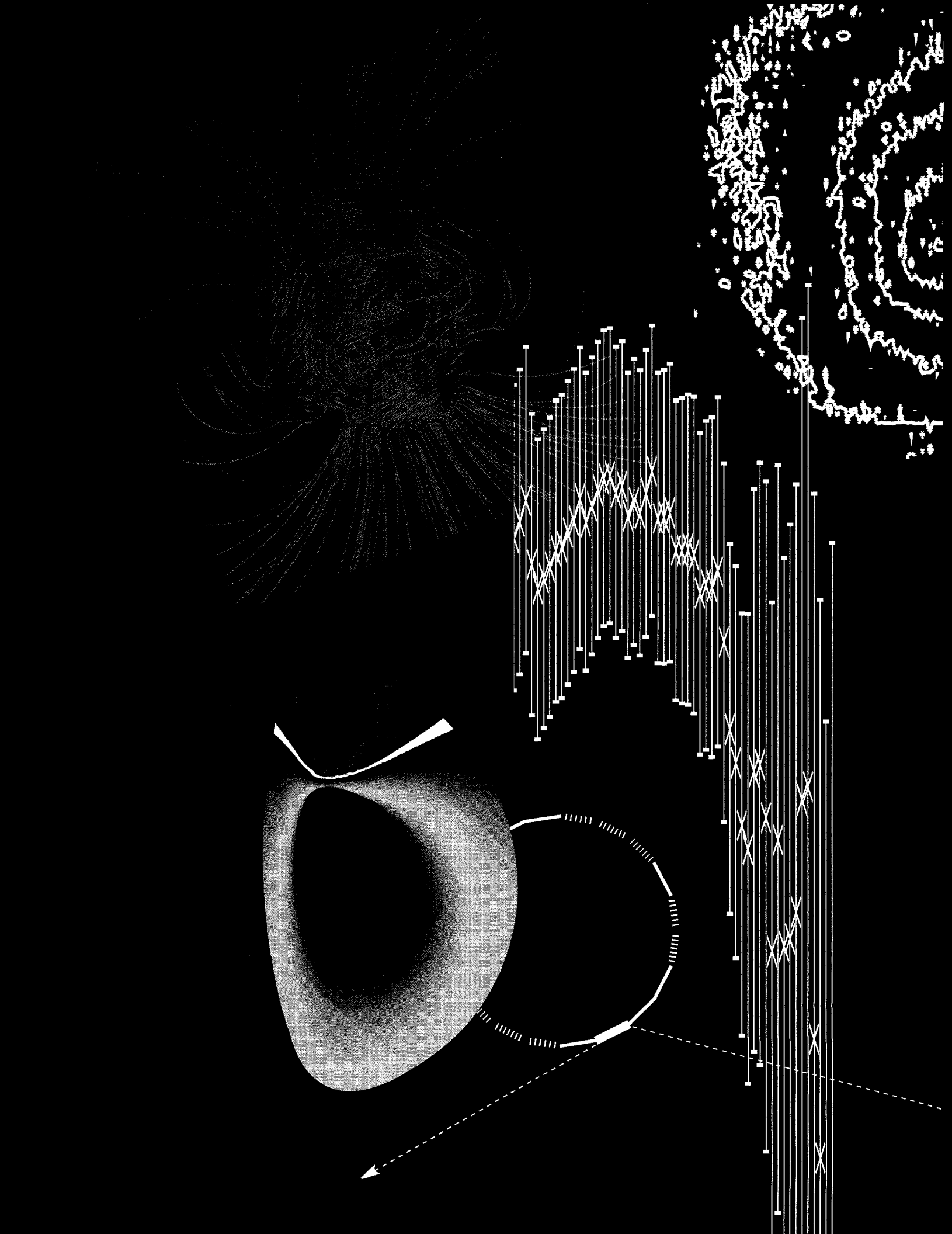
Using molecular self-assembly techniques, LDRD researchers have developed a compact, robust, surface-acoustic-wave-based chemical microsensor for remote, real-time sensing of volatile organic compounds. The microsensor is reversible and can be used to monitor continuously changing concentrations of a contaminant over an extended period of time. This capability is relevant to environmental monitoring of defense wastes and to detecting environmental indicators of weapons production.

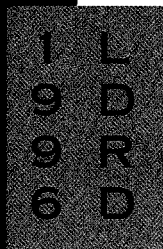
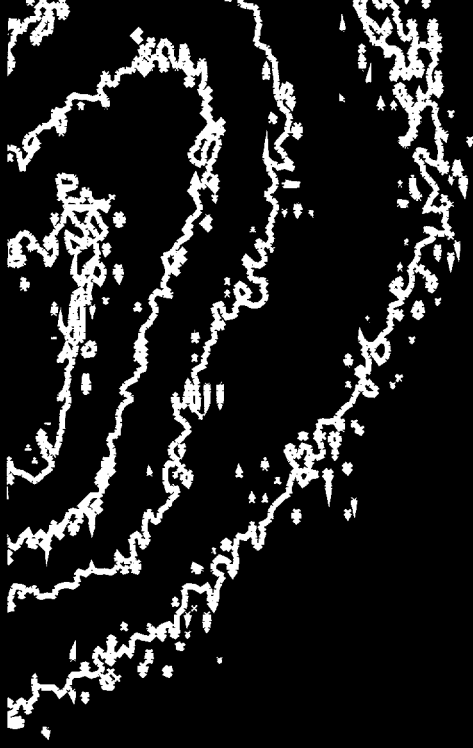
LDRD Project Summaries

In the following sections, we have grouped project summaries by LDRD component—IP, CD, and PD—and then subdivided them into nine technical disciplines:

Materials Science
Engineering and Base Technologies
Plasmas, Fluids, and Particle Beams
Chemistry
Mathematics and Computational Sciences
Atomic and Molecular Physics
Geoscience, Space Science, and Astrophysics
Nuclear and Particle Physics
Biosciences

A list of related publications written by project team members is included with the summaries. An index to the projects' principal investigators is provided at the end of this report.

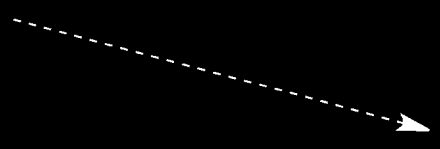




Individual Projects

Individual Projects (IPs) are staff-initiated R&D aimed at strengthening the Laboratory's science and technology base and fostering a stimulating research environment. These projects play a key role in maintaining the expertise and state-of-the-art technologies that underpin the Laboratory's scientific and engineering excellence. IPs accounted for 38% of this year's LDRD budget and 46% of all projects, and they supported research in all nine technical disciplines.

Examples of subjects investigated by IPs include nonlinear atom optics, dynamics of quantum wave packets, chemistry and catalysis in supercritical media, microsenors for volatile organic compounds, quantum cryptography, optical imaging through turbid media, nonlinear processes in earthquakes, three-dimensional climate models, nanoengineered films, phase stability of transition metals and alloys, particles and patterns in cellular automata, high-speed computer interfaces and networks, antiquark distributions in the proton, weak interaction measurements using optically trapped radioactive atoms, high-intensity laser-matter interactions, turbulence in complex fluid flows, the structure and dynamics of surface recognition, and the role of the telomere in birth defects.



Origin of Radiation Damage in Potassium Titanyl Phosphate

D. Wayne Cooke

Potassium titanyl phosphate (KTP) is the most widely used material for nonlinear optical applications such as optical parametric oscillators and laser frequency-doublers. However, its use is limited to low-power applications because of laser-induced damage incurred at high power. The origin of this damage is presently unknown.

Recent investigations of radiation damage in KTP showed that the material emits bursts of light upon heating or cooling over a broad temperature range (4–675 K). This emission is believed to result from the development of a large surface electric field that discharges into the ambient environment. The field evolves from a change in spontaneous polarization as a function of temperature, a phenomenon called pyroelectricity. This observation implies that laser excitation of KTP may cause a change in its temperature, thereby inducing large electric fields that might contribute to the optical-damage threshold in KTP. The consensus is that reduction of Ti^{4+} to Ti^{3+} ions in KTP is responsible for the damage and that two-photon absorption or other electronic mechanisms are involved.

We believe that laser-induced thermal mechanisms may be relevant. Specifically, our objective was to demonstrate that electrons could be produced in KTP by thermal rather than optical excitation. That is, excitation with a CO_2 laser, which has a wavelength 10 times that of a neodymium-based laser and therefore cannot excite electrons across the band gap, may in fact produce

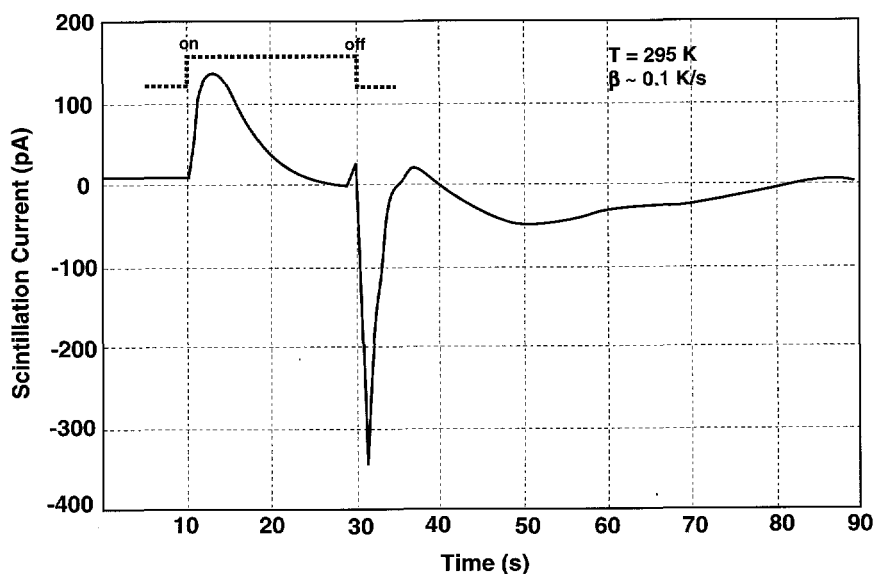
electrons via ionization as a result of the pyroelectric effect in KTP. We excited the KTP sample with CO_2 laser radiation and, with an optical multichannel analyzer, measured bursts of light coincident with the laser pulse. By attaching electrodes to two surfaces of the crystal, we also measured current pulses.

Shown in the accompanying figure is the current generated in KTP at 295 K by a CO_2 laser pulse. The maximum current occurs during the on-off cycle of the laser, which corresponds to the maximum change in the crystal's spontaneous polarization. Simultaneous with this peak current is the occurrence of optical bursts of light, implying surface

electric fields of approximately 30 kV/cm. These results agree with what we expected based on pyroelectricity in KTP; the surface field should be proportional to dP_s/dt or, equivalently, to $(dP_s/dT)(dT/dt)$, where P_s is spontaneous polarization, T is temperature, and t is time. From the second factor, dT/dt , we see that fields evolve from a large rate of change in temperature, as induced by the laser on-off pulse. Observation of pyroelectricity in KTP provides an important new insight into the possible origin of optical damage in these materials.

Publications

Cooke, D.W., B.L. Bennett, R.E. Muenchausen, et al., "Pyroelectricity and its Role in Radiation Damage of Potassium Titanyl Phosphate Crystals," in *Proceedings of the SPIE* (SPIE, Bellingham, Wash., in press).



Current generated in KTP at 295 K by a CO_2 laser pulse. The continuous-wave laser is turned on at $t = 10$ s and off at $t = 30$ s, as shown by the dashed profile. The approximate crystal heating rate during this time interval is 0.1 K/s.

Development of a Fundamental Understanding of Chemical Bonding and Electronic Structure in Spinel Compounds

Kurt E. Sickafus

Our objective is to investigate the role of chemical bonding and point defects (both extrinsic point defects and cation-disorder antisite defects) on structural stability and electronic structure in compounds with the spinel crystal structure. Experimentally, we assess structural and electronic properties of spinel samples using electron energy-loss spectroscopy (EELS) and electron, x-ray, and neutron diffraction techniques. We perform total-energy electronic-structure calculations to determine structural stability, band structure, density of states, and electron distribution.

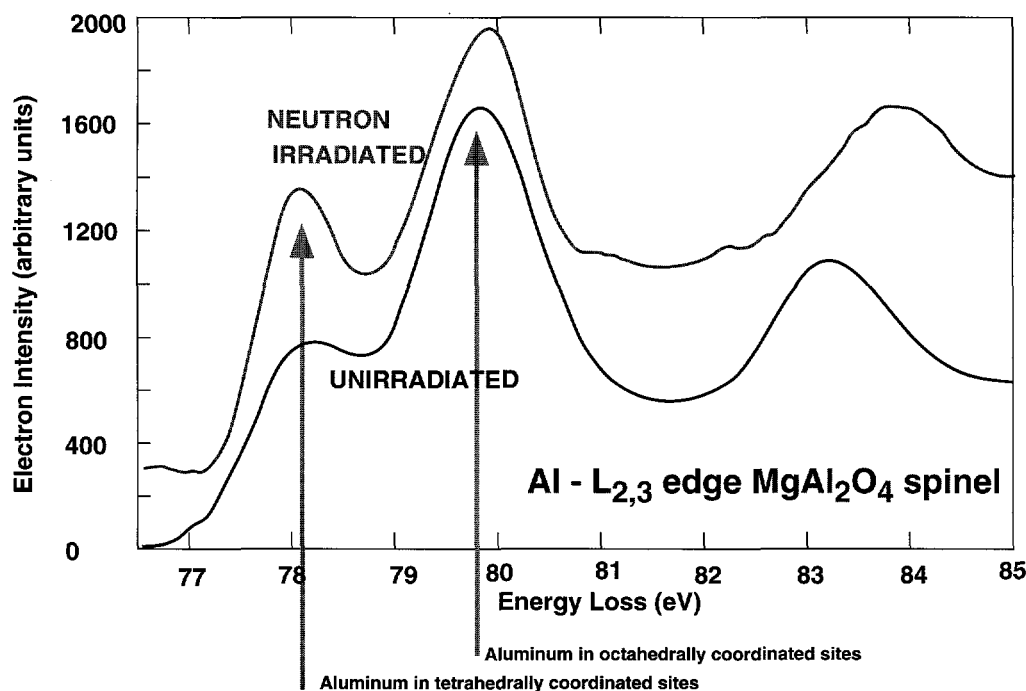
This year we prepared, by sol-gel synthesis routes, oxide compounds in

the composition field $\text{MgO} \cdot \text{Al}_2\text{O}_3$ through $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ from magnesium, aluminum, and chromium nitrate precursors. We are using these samples to measure electron-loss near-edge structure (ELNES) by the EELS technique (see plot of energy loss vs electron intensity). ELNES is proportional to the density of states at the bottom of the conduction band of the material being examined.

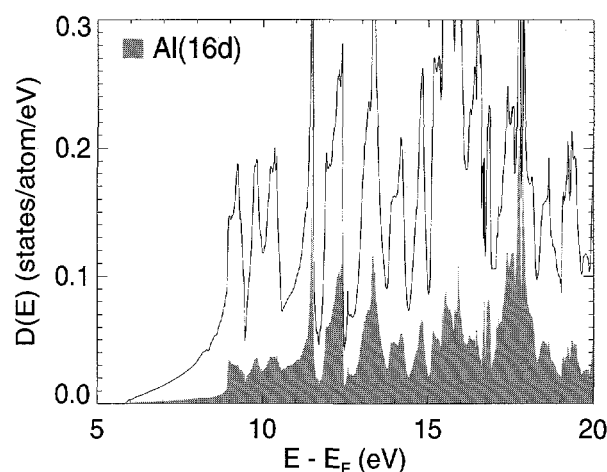
We performed neutron diffraction experiments on single crystals of stoichiometric (equimolar) spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) and nonstoichiometric (nonequimolar) single crystals of spinel ($\text{MgO} \cdot 3\text{Al}_2\text{O}_3$). Crystal-structure refinements of the diffraction data revealed that point defects

accommodating deviations from the equimolar spinel composition reside on both tetrahedral and octahedral cation sites.

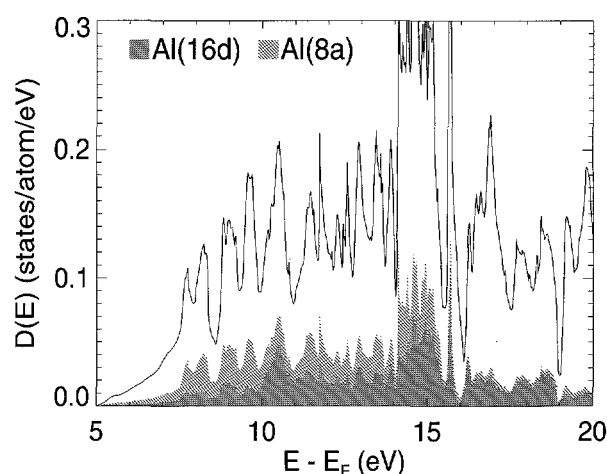
We completed total-energy electronic-structure calculations for $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and $\text{MgO} \cdot \text{Ga}_2\text{O}_3$ in both normal and inverse structures (see plots of $E - E_F$ vs $D(E)$ for $\text{MgO} \cdot \text{Al}_2\text{O}_3$). We demonstrated excellent agreement between theory and experiment in basic structural parameters. By analyzing the band structure, we have identified aluminum-related sp bands pulled down out of the valence band in the inverse structure as the source of the extra peak observed in the EELS/ELNES spectra.



EELS spectra obtained using a dedicated scanning transmission electron microscope. In these spectra we examine the ELNES in magnesio-aluminate spinel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$. The peak just below 80 eV is at the onset of the aluminum $L_{2,3}$ absorption edge and reflects the aluminum contribution to the density of states of the conduction band from octahedrally coordinated aluminum ions. Following neutron irradiation to a high dose, a substantial fraction of aluminum atoms in the lattice relocate from octahedral to tetrahedral sites. This relocation is manifested in EELS analyses by an enhancement of the ELNES peak at 78 eV. In a perfectly ordered, "normal" spinel crystal, this additional ELNES peak would not exist. Quantitatively, the occupation of tetrahedral sites by aluminum atoms increases from about 20% to greater than 50% following neutron irradiation.



Calculated valence site, $E - E_F$, vs projected density of states, $D(E)$, for the normal structure of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, wherein all of the aluminum cations reside on octahedrally coordinated lattice sites. Contributions to the density of states from the different lattice sites are indicated by the different shadings.



Calculated valence site, $E - E_F$, vs projected density, $D(E)$, of states for the inverse structure of $\text{MgO} \cdot \text{Al}_2\text{O}_3$. In this case the aluminum cations are distributed equally between octahedral and tetrahedral lattice sites. A prominent new feature in the density of states for inverse spinel appears near 8 eV. This structure is absent in the density of states for normal spinel. It is probable that this new band of states arises primarily from tetrahedral aluminum and is responsible for the additional peak that we observe in the ELNES spectra at 78 eV.

Phase Stability of Transition Metals and Alloys

Robert Hixson

Our objectives were to study the phase transitions in transition metals and to attempt to move the transition pressure by alloying with d-electron donor metals. Such a study will lead to a better understanding of the phase diagrams of both pure transition metals and alloys. Furthermore, this study is essential for a complete understanding of the physical properties of materials under varying conditions. We also made progress in the areas of theory, metallurgy, and experiment.

Theory. We have calculated the virtual crystal approximation of the

structural stability of pure titanium and its alloys. The results confirm the first year's results that the omega phase occurs as a result of one-electron band filling. As compared with Ti-V alloys, tantalum and tungsten decrease the structural transition pressure.

Metallurgy. We have prepared samples of hafnium and molybdenum alloys. In addition, we prepared samples of Mo-Re (10%), Mo-Re (30%), and Mo-Re (40%) with sufficiently fine grain structure to be used in the diamond anvil cell (DAC).

The Mo-Re (40%) buttons shattered upon rolling as a result of the presence of sigma-phase material. Samples of Hf-Nb (1%), Hf-Nb (3%), and pure hafnium were produced.

Experimental. Our work has continued on defining the alpha-to-omega transition pressure in pure titanium, which has turned out to be more difficult than anticipated. Pure titanium and the Ti-V material studied in previous years have very close to the same free energy, and our experimental work shows a very similar alpha-omega transition pressure. Because this result was surprising, we have spent the last year perfecting our technique for growing single crystals in the DAC. This work shows a transition pressure close to 90 kbar for both pure metal and Ti-V alloy.

Theoretical and Experimental Investigation on the Low-Temperature Properties of the NbCr_2 Laves Phase

Dan Thoma

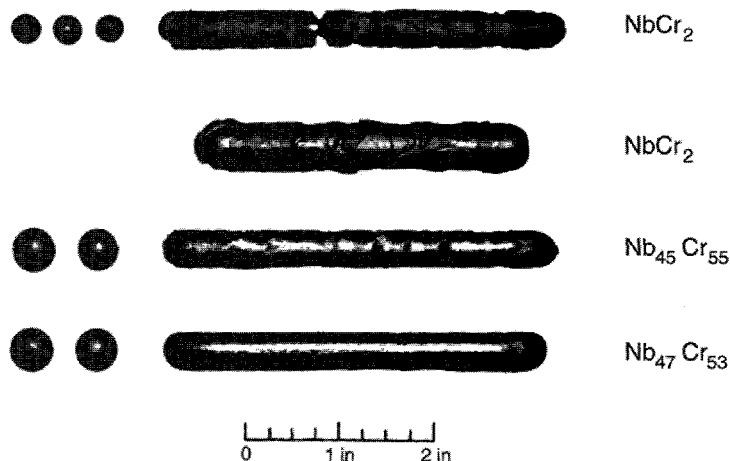
Laves phases are the most abundant yet least utilized intermetallic phases. Because of some unique properties (including superconductivity, magnetic properties, hydrogen-storage characteristics, high melting temperatures, high strength, reasonable oxidation resistance, and excellent creep properties), they have unusually high potential for a wide variety of applications that are directly related to energy sciences. For example, in addition to high-temperature structural applications (heat exchangers for coal conversion and gas turbine engine materials), Laves phases also have significant nonstructural applications: $(\text{Tb,Dy})\text{Fe}_2$ is used as a magnetoelastic transducer because of its giant magnetorestriction, $(\text{Hf,Zr})\text{V}_2$ has been used for special superconductivity requirements, $\text{Zr}(\text{Cr,Fe})_2$ has been utilized for hydrogen-storage applications, and the $\text{Mo}(\text{Co,Si})_2$ Laves phase contributes to the wear-resistance of "Tribaloy" materials. Unfortunately, the overall potential of Laves phases has not been exploited, largely because of their tendency for low-temperature brittleness.

We are focusing on experimental and theoretical alloy design methodologies in order to elucidate and optimize deformation mechanisms as a function of defect structure for the C15 Laves phase NbCr_2 (C15 refers to the crystal structure). Our results should provide a scientific methodology—from atomic to bulk scale—that will improve the low-temperature ductility and toughness of Laves phases. As a result, an increased application of the largest class of materials will be available for a variety of energy-related technological fields.

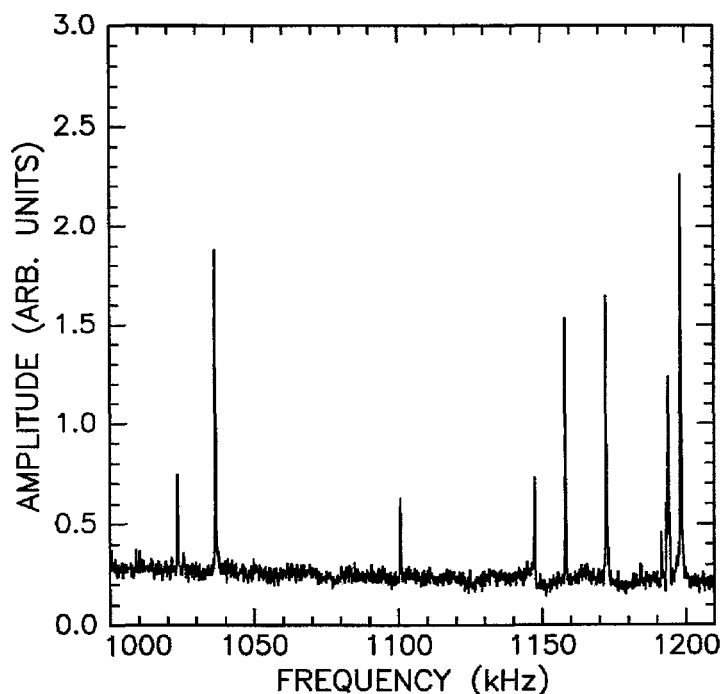
We have made substantial progress in the past year to achieve these project objectives. Our accomplish-

ments include (1) preparing materials for single-crystal growth and mechanical testing (see photograph),

(2) measuring physical properties such as elastic parameters (see accompanying spectrum),



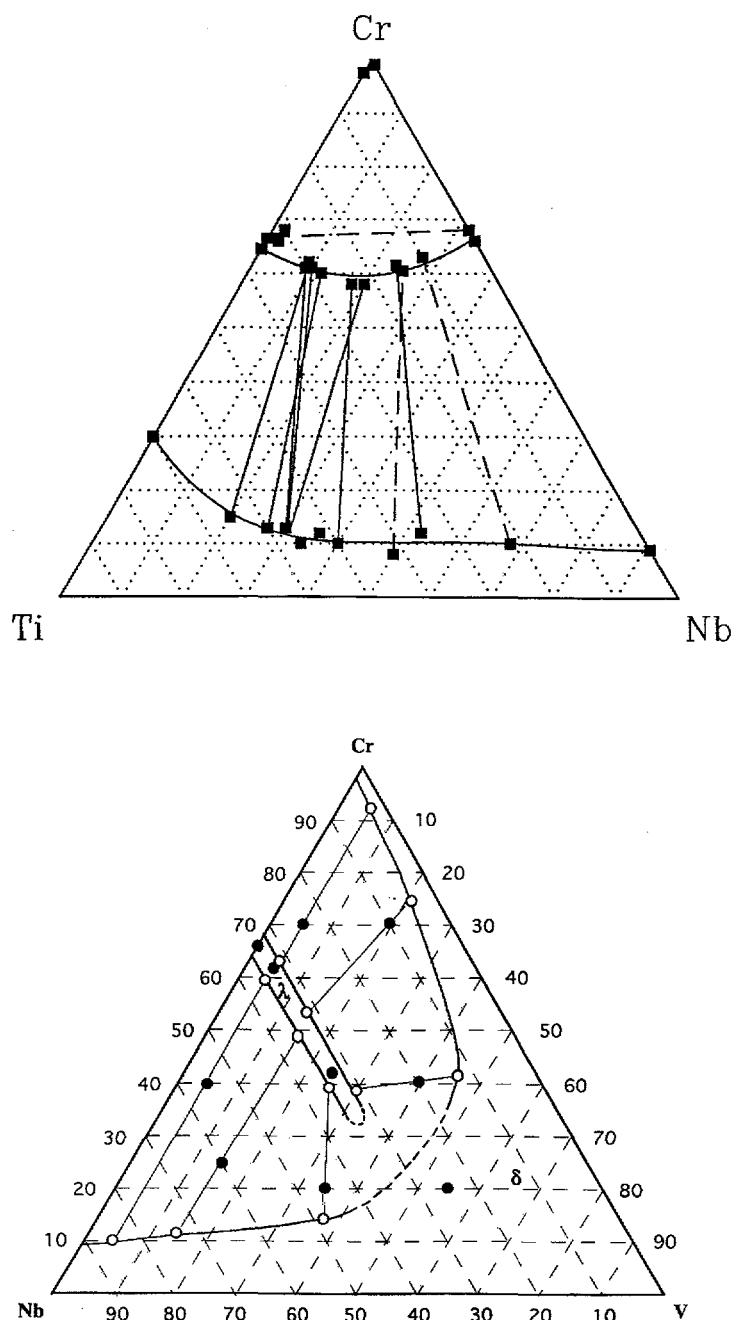
Arc-melted buttons and rods of NbCr_2 and NbCr_2 -based composites.



A portion of a resonant ultrasound spectrum of C15 NbCr_2 taken at room temperature. This spectrum is used to determine the elastic parameters of C15 NbCr_2 . The units of amplitude are arbitrary.

(3) establishing ternary phase diagrams for Nb-Cr-M (M = Ti, V, and Be), such as the two diagrams shown, (4) determining the defect structures/mechanisms and alloying behavior in C15 NbCr₂-based Laves phases, (5) performing first-principles

total-energy and electronic-structure calculations for the C15 NbCr₂ Laves phase, and (6) developing an alloy design scheme for the C15 NbCr₂ Laves phase based on the combined experimental and theoretical investigations.



Ternary phase diagrams of Nb-Cr-Ti and Nb-Cr-V, indicating the phase field of the ternary Laves phase based on NbCr₂.

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Nanostructured Materials: Growth and Patterning Using Hyperthermal Materials Chemistry

Mark Hoffbauer

In the next century, high-density compact disks, large and bright flat-panel displays, fast computers, and many other microelectronic devices will rely on our ability to produce nanostructured thin-film materials. These thin-film materials are produced atom-by-atom for the purpose of controlling their atomic-layer properties. Our research goal is to produce nanostructured thin-film materials that will make electronic and optical products run longer, faster, and more efficiently than those presently available.

At the Laboratory, we have recently developed a facility for producing nanostructured thin-film materials using hyperthermal materials chemistry, in which we selectively activate desired chemical reactions using the kinetic energy of one or more key atomic species incident upon a thin-film surface. The advantage of hyperthermal materials chemistry is that coveted electronic materials can

be easily produced at low surface temperatures, avoiding common problems such as thermal degradation, defect formation, and chemical impurities that are associated with existing high-temperature processes.

We are using hyperthermal materials chemistry to grow wide-band-gap, thin-film nitride materials (such as gallium, indium, aluminum, and carbon nitrides). Using a beam of high-kinetic-energy nitrogen atoms, we have grown gallium nitride films on GaAs. Analysis of these films using x-ray photoelectron spectroscopy has shown that nitrogen completely replaces the arsenic. Early indications are that we have synthesized thick gallium nitride films (>20 nm) of very high quality at low surface temperatures.

We have also grown nitride films at low surface temperatures on indium, aluminum, silicon, diamond, and sapphire surfaces. Our preliminary analysis indicates significant nitrogen

incorporation into the surfaces in spite of the thick oxide layers already present on some of the surfaces. For example, thick nitride films grow on indium and aluminum surfaces, and silicon forms silicon nitride and silicon oxynitride. Detailed analysis of the quality of these nitride films will enable us to further optimize the growth process. Analysis of the diamond surfaces indicates that we have incorporated significant amounts of nitrogen into the surface. If further analysis demonstrates that we have formed a crystalline carbon nitride film, we will be the first to have synthesized this substance, which is theoretically predicted to be harder than diamond.

We have achieved significant progress toward improving nitride thin-film growth using hyperthermal atoms. The next step will be to process selected areas of materials using direct patterned thin-film growth and etching. These processes are necessary for electronic device production. Our goal is to use hyperthermal atom beam sources to perform carefully controlled processing on length scales of <100 nm. We will then be able to create nanostructured devices of unprecedented quality.

Inorganic-Organic Composite Nanoengineered Films Using Self-Assembled Monolayers for Directed Zeolite Film Growth

Robert Dye

The objective of the project is to attempt the directed growth of a zeolite (aluminosilicate) cage crystal from an organic template deposited as a Langmuir-Blodgett (LB) film on a silicon wafer substrate. This work supports fundamental research on materials synthesis of an inorganic material from a tailored organic precursor film (biomimetic synthesis). We ran two phases of this project concurrently: synthesis of the target amphiphile containing a quaternary

ammonium group which could nucleate the crystallization of ZSM-5 zeolite, and preparation of LB films of selected model compounds onto a treated silicon wafer.

We took the organic synthesis of a monosubstituted norbornadiene trimer to the ethyl carboxylate stage. Then we developed a large-scale synthetic method to make the norbornadiene trimer in good yield, using selective sublimation and recrystallizations to obtain pure trimer from a mixture of

dimer, trimer, tetramer, and their isomers. We prepared the ethyl carboxylate as the precursor to further chemical reactions which should produce the targeted quaternary ammonium salt. Several attempts at producing the free carboxylic acid failed. Our last try was only moderately successful.

Deposition of LB films using equipment at the Advanced Materials Laboratory in Albuquerque resulted in high-quality films that could be used for our purposes. Under appropriate reaction conditions, we used one of these model films to produce what appeared to be ZSM-34 zeolite on the surface. Making the experiment safer by using a high-pressure bomb instead of a sealed glass jar resulted in our not being able to reproduce the first success.

Rigid Molecular Foams

Warren P. Steckle

Carbon foams have been finding many applications in recent years. Applications include fuel-cell electrocatalysts, general catalyst supports, porous adsorbents, and foam electrodes for use in batteries and capacitors for energy efficiency and conservation. We prepared a series of rigid hypercrosslinked foams, using simple, rigid polyaromatic hydrocarbons such as benzene, biphenyl, m-terphenyl, diphenylmethane, and polystyrene, with p-dichloroethylene as the crosslinking agent. After drying the gels, we found the resulting foams robust and rigid. Their densities range from 0.3 to 0.5 g/cm³. Upon carbonization the densities of these foams increased to a range from 0.6 to 1.0 g/cm³.

As catalyst supports, these carbonized foams can retain their integrity

and porosity to temperatures greater than 1,000°C in nonoxidizing atmospheres. We also investigated the hypercrosslinked foams and the carbonization of these materials for their ability to chelate metals.

We prepared polymeric crown ethers by the polycondensation of dibenzo-18-crown-6. Crown ethers can chelate certain metals within their ring. Supported crown ethers have been of interest for the past several years in environmental clean-up and remediation. We also prepared other potential candidates for metal uptake by the sulfonation of other aromatic hypercrosslinked foams. To elucidate the structure of these hypercrosslinked materials, we used nitrogen-adsorption, surface-area analysis, transmission electron microscopy, and solid-state, nuclear magnetic resonance

experiments. Pore size distributions ranged from 5 to 1000 Å, depending on starting materials.

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Materials Research for Optical Refrigeration

Richard Epstein

Our objective is to characterize and test a variety of crystals and glasses for their usefulness as optical refrigerants. Depending on the operating conditions to which they are subjected, numerous materials can be useful optical refrigerants. In particular, the optimal refrigerant material will depend upon operating temperatures and type of diode lasers used. Our research is significant because of its great potential for allowing the development of cryocoolers that operate efficiently between a few tens of kelvins up to food-freezer temperatures.

This year, we confirmed theoretical predictions that some ytterbium-doped fluoride glasses may effectively cool at

100 K. This was the first demonstration of a solid-state cooling process that works below 150 K, and it laid the groundwork for developing a practical cryogenic device. Additionally, we have created a list of candidate cooling materials that may be superior to ytterbium-doped fluoride glasses. In particular, we are looking for materials that will cool at lower temperatures and have better thermal and mechanical properties than ytterbium-doped fluoride glasses. We have characterized the spectral properties of seven materials (five ytterbium-doped crystals, an ytterbium-doped glass, and ruby). We found that one material, BaYYbF, has

very promising absorption and fluorescent spectra. The initial calorimetric measurements, however, showed that the particular sample we were studying does not cool at room temperature because of impurity contamination. We will be working to correct that problem by using purer BaYYbF crystals in our experiments.

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Innovative Composites through Reinforcement Morphology Design—A Bone-Shaped Short-Fiber Composite

Yuntian T. Zhu

The objective of this project is to improve the strength and toughness of conventional short-fiber composites by using innovative "bone-shaped," short fibers as reinforcement. We have made significant progress in the fabrication and characterization of a prototype composite and in the understanding of the toughening mechanisms through numerical modeling. Our accomplishments on the experimental front include the following: (1) We have demonstrated that the strength and toughness of a bone-shaped, short-fiber composite improve by 34% and 200%, respectively, over that of a conventional short-fiber composite (as shown in the first figure). (2) We have automated the fabrication of bone-shaped fibers with a fiber production rate of 2400/h. (3) We have established a procedure to form nodules along Nicalon fibers (see second figure). When chopped, these nodular Nicalon fibers play a similar role as the bone-shaped fibers. (4) We have established a facility and procedure to make composite samples with short fibers randomly distributed and aligned as in the third figure.

Using the finite-element method (FEM), we are studying the load-transfer mechanism of bone-shaped fibers and searching for better fiber geometrical design. We have found that there is a critical fiber length above which bone-shaped fibers are superior in strength as compared with straight-fiber composites.

On the modeling front, we have tailored the composite lattice spring failure-analysis model (CLASFAM) to facilitate both chopped, straight, and bone-shaped fibers randomly distributed in an elasto-plastic matrix with fiber failure strength following the Weibull distribution. We accounted for the fiber shape in the model by using

different load-transfer functions as determined by FEM.

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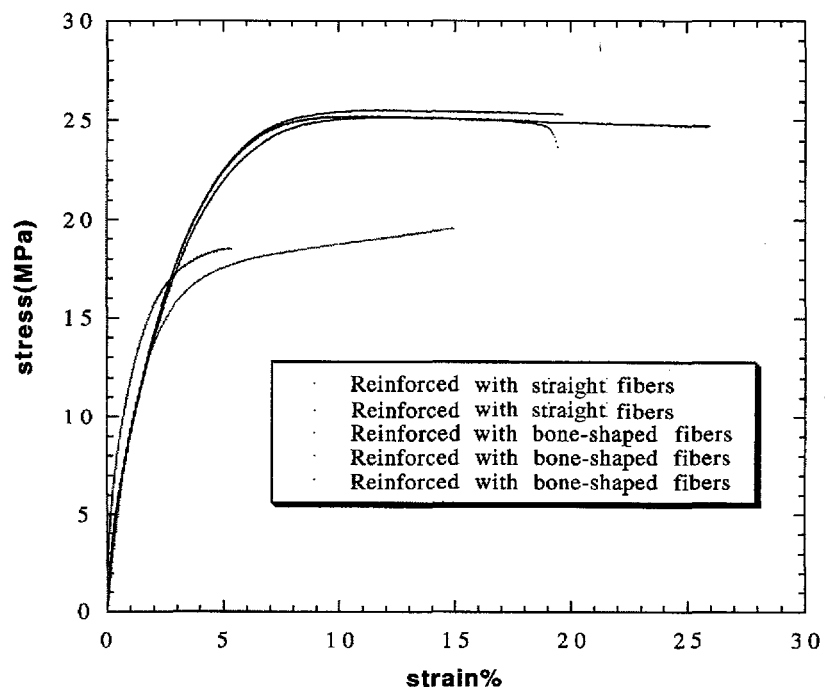
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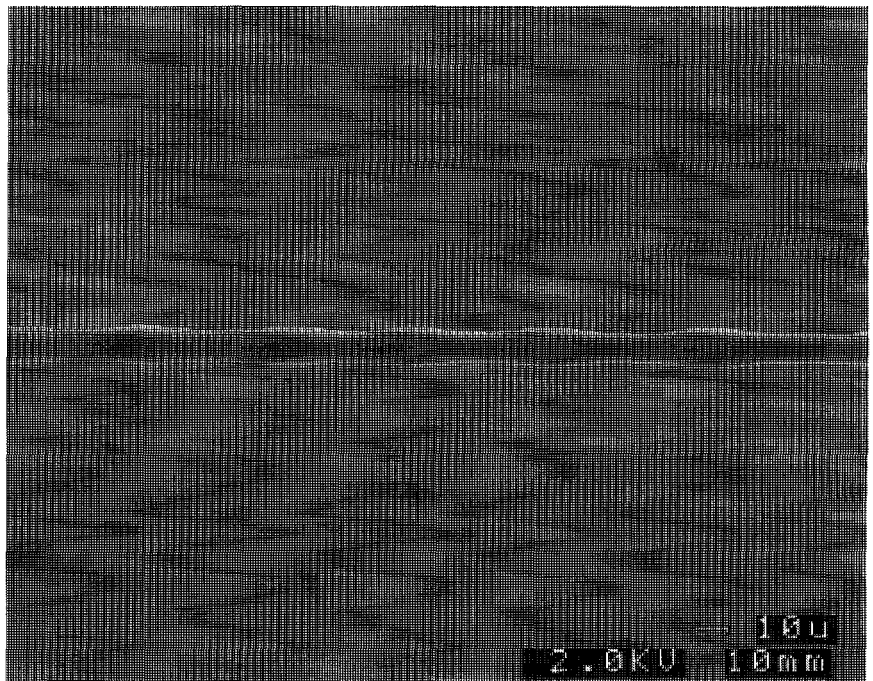
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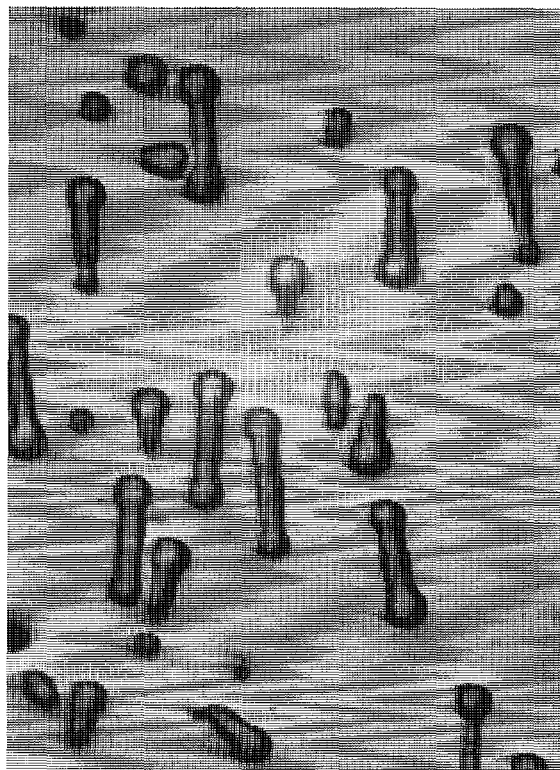


Stress-strain curves of composite samples, which are made of polyester matrix reinforced with straight nickel fibers (bottom two dotted lines) or bone-shaped nickel fibers (upper three solid lines). Nickel fiber length = 2.5 mm, diameter = 76.2 μ m, and fiber volume fraction = 3.3%. The average strength and toughness (area under the stress-strain curve) of the bone-shaped, short-fiber composite samples improve by 34% and 200%, respectively, over that of conventional short-fiber composite samples.

A Nicalon fiber with nodules obtained by high-temperature oxidation of commercial Nicalon fibers.



Fibers are aligned and randomly distributed in a glass-fiber-reinforced, polyester-composite sample.



New Deposition Processes for the Growth of Oxide and Nitride Thin Films

Kevin Hubbard

The general goal of this effort is to apply an integrated approach to develop and understand the details of the deposition process for metal oxides and nitrides from homoleptic metal amido precursors. This understanding will lead to new routes for the production of high-quality materials that have wide application. Organometallic chemical vapor deposition (OMCVD) has been slow in gaining acceptance for coatings applications despite the possibilities for significant advantages over metal-halide-based CVD processes. The major underlying limitation is the lack of understanding of the chemistry important to the deposition process.

Control of the fundamental chemistry of a deposition process is the key to advancement of the OMCVD technique.

Recently, the efficient transamination of homoleptic metal amides $[M(NR_2)_x]$ with ammonia to yield highly reactive metal amido/imido intermediates has been used to develop low-temperature, high-growth-rate processes for the deposition of high-purity metal nitrides and oxides. The purpose of this project is to improve our understanding of the deposition mechanisms for these precursors and to expand the list of technologically important materials that can be deposited from them.

This year we successfully completed a low-pressure CVD reactor for the deposition of pure and doped GaN thin films and synthesized homoleptic amido precursors for the Ga and for the Zn dopant. We also successfully deposited pure and Zn-doped GaN films at low temperatures (250°C–550°C) and developed synthesis routes for homoleptic amido precursors for the deposition of AlN, InN, and In_2O_3 , as well as their alloys. TiN and Zr_3N_4 were deposited using plasma-enhanced CVD. We deposited the TiN on Kevlar fibers to improve their performance under compressive stress and studied Zr_3N_4 for its dielectric properties.

Publications

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Texture Characterization for HE Design

Sheila Schiferl

The objective of this project is to develop the capability to investigate the effects of crystallographic texture (the preferred orientation of single-crystal grains in a polycrystalline material) on the behavior of high-explosives (HEs). Preferred orientations are consequences of metal-working and other thermomechanical processes and result in both strength and elastic anisotropies. This research includes three components: state-of-the-art survey, model development, and implementation of models in design code. Our research will improve the predictive capabilities that became an essential part of stockpile stewardship after underground nuclear testing was banned.

We used crystallographic-texture modeling concepts from both the

open and secure literature, and we extended methods that we had developed for conventional weapons. In our modeling, textured materials are treated as polycrystals. Individual grains deform by shears on several slip systems (a slip system is composed of a particular shear plane plus a particular direction in that plane), each slip system has a critical stress, and a maximum work criterion selects five independent systems. For a given strain, the model obtains the tensor yield strength by averaging the stresses over all the grains and then fits the resulting yield "points" to an analytic function. The textures we investigated are typical for processing weapons materials. We normalized the yield functions using experimental data.

We can adapt these techniques to anisotropic elasticity by averaging elastic constants over the grains. We incorporated a texture-based model of anisotropic strength into a two-dimensional Lagrangian code. Capabilities of this new code include an axisymmetric polar decomposition for rotations, a directional yield function, and a geometric-"normal" iterative return to the yield surface that is performed in a fixed material frame.

Publications

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Interfacial Charge Transport in Organic Electronic Materials: The Key to a New Electronics Technology

Darryl Smith

Organic electronic materials and devices are poised to revolutionize major technological areas, such as information display and optical communication, because of their processing advantages, the tunability of their electronic properties, and their materials and design flexibility. We can make the complex structures necessary for the technology cheaply and easily. We can modify the electronic properties of these materials in a controlled way by making systematic changes in their molecular structure. We would have many design options at both the molecular and mesoscopic scales for organic electronic materials and devices if we had a better fundamental understanding of their properties. Because interfaces are the essential active elements in every organic electronic

device, we must understand interfacial charge transport to realize the potential of these materials and devices. Our primary goal is to develop this basic scientific understanding.

In this first year of the project, we have developed a theory to describe the electronic structure of metal/polymer interfaces. This theory predicts the behavior of Schottky energy barriers at these interfaces. We have also taken a series of electroabsorption and internal photoemission measurements on interfaces between the conjugated polymer MEH-PPV (a derivative of poly[phenylene vinylene]) and a series of metals. We were able to successfully interpret these measurements in terms of our theoretical model.

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Thermodynamic and Electrodynamic Studies of Unusual Narrow-Gap Semiconductors

Albert Migliori

Cryogenic solid-state refrigerators based on the Ettingshausen effect (heat transport by carriers in a magnetic field) can provide vastly superior performance to Peltier devices, and can thus create new markets in electronics, superconductor, and medical applications. The goals of this project are to design and create new materials, to study their transport and thermodynamic properties to determine if they are appropriate for such devices, and to optimize their performance. Our specific

objective is to select from such materials those of highest performance. In parallel we are developing a comprehensive theory to be used to tune the selected systems (Bi-Sb systems) to produce maximum transverse thermopowers below 200 K.

We have eliminated many of the hybridization-gap semiconductors and skutterudites from consideration and discovered a possible new explanation for the high mobilities in Bi-Sb alloys that may make certain little-studied

variants the best choices for an Ettingshausen cooler. We have also advanced the state of the theory of the Ettingshausen effect and have shown it to be fundamentally different from the Peltier effect. Ettingshausen coolers, unlike Peltier coolers, can approach Carnot efficiency when phonon thermal conductivity is controlled. We have also constructed and used an apparatus to make all the necessary measurements. These measurements (resistivity, Hall resistivity, thermopower, transverse thermopower, and thermal conductivity) were made on single crystals of Bi, Bi-2%Sb, Bi-8.5%Sb-0.05%Sn, Bi-14%Sb, SmB₆ and other materials. We found astonishingly high transverse thermopowers in BiSb alloys at small magnetic fields (less than 2 T) at temperatures near 50 K.

A Molecular Architectural Approach to Novel Electrooptical Materials

DeQuan Li

Optical devices are used in a variety of applications, including optical computing, data storage, and optical communication. A number of optical devices contain electrooptical (EO) materials—materials in which applying an electric field changes the indices of refraction—that are used to manipulate light. Improving the performance of EO materials, and thus increasing the amount of information transmitted by the optical devices, is a constant concern.

The goal of our project is to construct polar multilayers with EO coefficients much larger than those of classical inorganic crystals such as potassium dihydrogen phosphate or quartz. Our approach incorporates ionic and covalent bonding among layers that contain preassembled chromophores—highly aligned dipole arrays that have stable and efficient EO properties. Furthermore, we intend to determine the fundamental mechanisms controlling the formation of polar self-assembled multilayers so that we can design advanced materials with high performance.

In this first year, we focused on the fundamentals of molecular self-assemblies, in which molecular components spontaneously organize into ordered structures. These fundamentals included the efficient interlayer bonding, the functionalities within molecular building blocks, and new techniques for monitoring multilayer growth. We took two approaches to tackle the interlayer bonding issues: (1) covalent bond formation at mild conditions and (2) multiple electrostatic-charge interactions between layers.

First, we synthesized various long-chain surfactants [$\text{BrCH}_2\text{-(CO)-O-(CH)}_{11}\text{-SiCl}_3$ and $\text{BrCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_{16}\text{-SiCl}_3$]. The advantages of these surfactants are that the active bromine group can react with pyridyl groups at room temperature and that the long alkyl chains will provide in-plane ordering effects in the self-assembled monolayers. Second, we carried out the multilayer growth by alternating an electron-rich building block, nickel phthalocyanine tetrasulfonate (NiPc), with a slightly electron-deficient building block, poly(diallyldimethyl)ammonium (PDDA). The ionic bonds formed very rapidly. We were able to manually grow thin films of NiPc and PDDA with as many as 100 bilayers (x-ray reflectivity/thickness = $\sim 0.08 \mu\text{m}$; spectroscopic ellipsometry/ $n_{\text{film}} = \sim 1.7$). The accompanying plots show the x-ray reflectivity data from four of our films.

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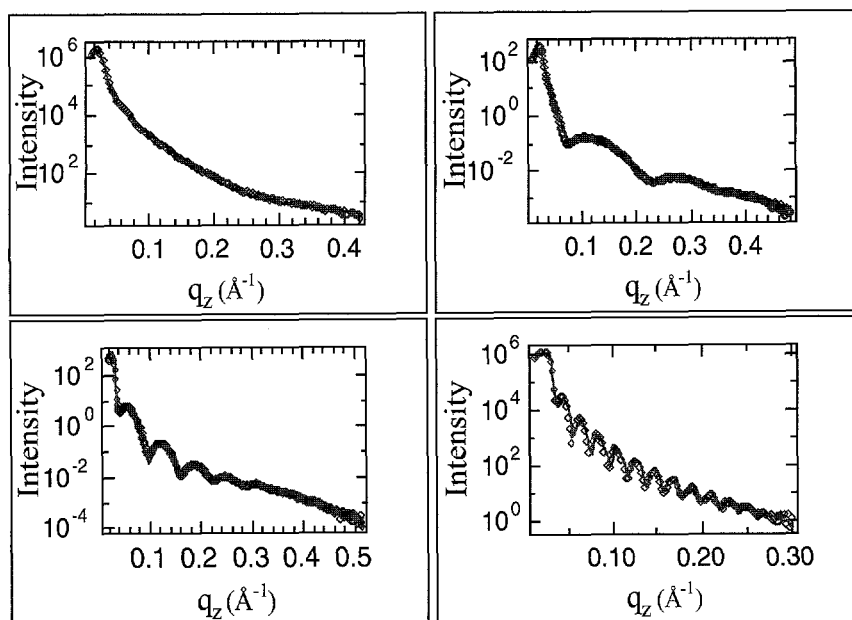
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X-ray reflectivity data (diamonds) and theoretical fit (solid line) for the substrate (top left), 3 bilayers (top right), 9 bilayers (bottom left), and 27 bilayers (bottom right). The vertical axis measures the intensity of the reflected x-ray, and the horizontal axis measures the momentum (q_z) of the x-ray along the z-direction. The number of fringes clearly increases as the number of layers increases.

Characterization and Manipulation of Broken-Symmetry Materials at Phase Boundaries

Robert Donohoe

The goal of this project is to understand the magnetic properties of low-dimensional materials. Magnetic parameters can help determine both the ground- and defect-state properties and the photodynamics of solid-state materials. These measurements can reveal important physical properties that we can relate to the chemical composition of materials and thereby better control a material's electronic and photophysical properties.

Our focus is to gain a fundamental understanding of ground-state instabilities induced in the spin density wave (SDW) and weak charge density wave (CDW) materials by the application of magnetic fields. We have primarily used Raman/magnon

scattering from samples in the bore of the 20-T magnet at the National High Magnetic Field Laboratory at Los Alamos in this investigation.

We are attempting to manipulate SDW or other non-Peierls distorted quasi-one-dimensional solids composed of halogen-bridged linear chains (MX) into new ground states by applying concerted and independent variations of the temperature and magnetic field. The experimental approach includes the detection of inelastic scattered light from the MX materials within a magnetic field with the objective of detecting phase transitions by observation of changes in Raman vibrational features and magnons.

We examined both of these features for a weak CDW material (PtI) and for the SDW NiBr MX chain. In neither instance was there a clear indication of phase transition as a function of applied magnetic fields (0–18 T). We could not conclusively demonstrate detection of a magnon in the NiBr material, although we observed a weak, broad band near 1500 cm^{-1} that exhibited some temperature dependence in accord with the expected behavior for such an excitation.

Engineering and Base Technologies

Development of New and Efficient Hard-Rock Mining Methods Using Pulsed-Laser Excavation

David Cremers

We are investigating the application of pulsed lasers to hard-rock mining. We believe that pulsed-laser excavation will be a more efficient method of hard-rock mining than either conventional mining methods or inefficient laser techniques based on thermal processing. The new pulsed-laser techniques that we investigated include hydraulic trapping of laser pulse energy at the rock surface (laser pulse/hydraulic effect) and resonant amplification of the shock waves induced through repetitive pulsing. We are also working to develop a method to deliver high-power laser pulses through a fiber-optic cable. We will in part use the results of this work to design a hard-rock mining instrument based on pulsed-laser excavation.

This year we investigated the effect of sampling geometry (lens focal length, angle-of-incidence, lens type, and lens-to-sample distance) on the coupling of laser-pulse energy in a solid matrix (soils and metals). Sampling geometry has practical applicability to laser-based hard-rock mining. We found that the laser plume temperature, emissions signals, and mass ablated from the solid were strongly dependent on geometry, and we determined the optimum values of these parameters.

We also investigated energy coupling into a solid sample located under water. Our experiments verified that a water layer several millimeters

thick produced strong coupling of the laser-pulse energy into the sample. This strong coupling efficiency produced high rates of material ablation. On the other hand, high laser-pulse repetition rates reduced energy coupling because the formation of bubbles on the surface duplicated laser ablation in air, which

characteristically has low rates of material ablation.

Publications

Multari, R.A., L.E. Foster, et al., "Effect of Sampling Geometry on Elemental Emissions in Laser-Induced Breakdown Spectroscopy," *Appl. Spectrosc.* **50**, 1483 (1996).

Pichahchy, A.E., D.A. Cremers, and M.J. Ferris, "Elemental Analysis of Metals Under Water Using Laser-Induced Breakdown Spectroscopy" (to be published in *Spectrochimica Acta B*).

Virtual Reality and Telepresence Control of Robots Used in Hazardous Environments

John W. Elling

The objective of this project is to develop virtual reality and telepresence control for robots used in hazardous environments. Such control of manipulators would allow operators to work on hazardous materials while being completely removed from the danger of exposure. However, the simulated environment in which the operators would work must be as representative of the actual hazardous environment as possible. Our method allows for component-based generation of software, which greatly reduces system implementation and development costs.

We developed a method to incorporate learning and adapting capabilities into traditional rule-based descriptions of environments. The learning and adapting capability is critical to robot programming for highly unstructured and variable environments such as inside glove boxes. We based our method on a hybrid expert system technology called expert networks and developed it with the associated knowledge capture techniques. Users will be able to apply our method to established simulation packages for virtual reality and telepresence control.

Nuclear Magnetic Resonance Imaging with Hyperpolarized Noble Gases

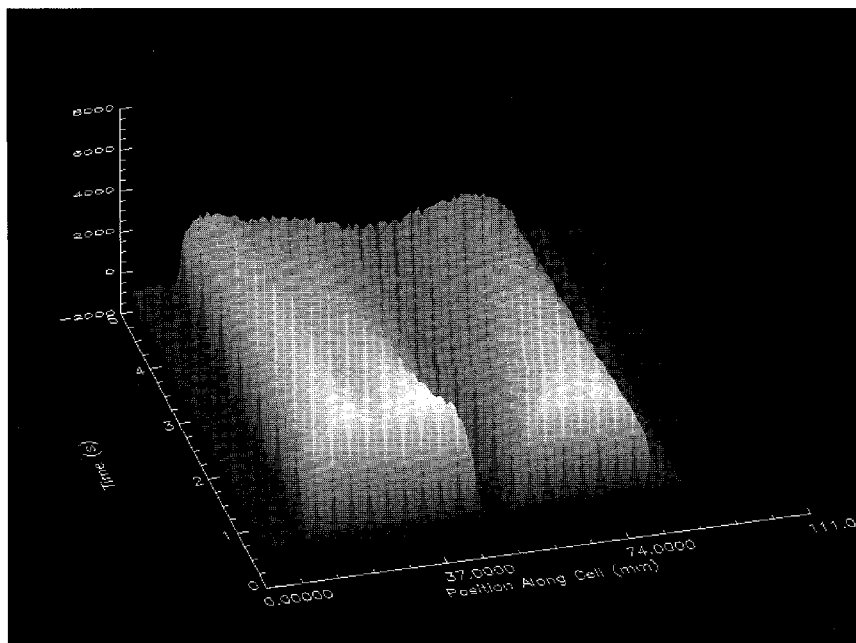
David Schmidt

Our objective is to demonstrate nuclear magnetic resonance (NMR) imaging of gas pressure distributions or porosity size distributions of objects containing a noble gas. In conventional magnetic resonance imaging (MRI), the signal is derived from nuclei that are thermally polarized in the presence of a large magnetic field. In contrast, the nuclei of noble gases can be hyperpolarized through laser-driven spin exchange. Furthermore, these gases have both a strong signal and a large diffusion coefficient. We exploited this fact in two different experiments and made great progress in our goal of demonstrating diffusion imaging.

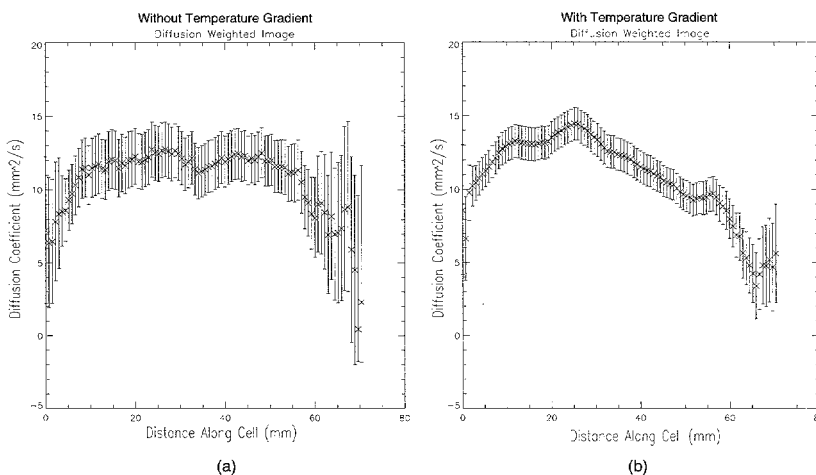
First, we inverted the polarization in a thin central section of a cylinder of hyperpolarized ^3He gas and made a series of one-dimensional (1-D) images of the cylinder over time in order to see the diffusion of the two populations of nuclei (see first figure). We measured a diffusion coefficient of $D = 12.3 \pm 0.2 \text{ mm}^2/\text{s}$.

The second experiment was to make diffusion-weighted images of the gas. We calculated a diffusion coefficient at each point in the image by taking the ratio of the image intensities with and without a previous magnetic field gradient in place. We show this process in the second figure, where the effects of temperature and of boundaries are reflected in the diffusion images.

Just as the relaxation parameters T_1 and T_2 are used to highlight differences in physical environments in NMR and MRI, we believe that the diffusion coefficient D can be used to highlight environmental differences. Possible applications include characterizing porosity of materials and dynamically imaging pressure distributions in biological or acoustical systems.



The series of 1-D images of the ^3He gas in the cylinder over a period of 5 s, one image every 0.2 s. The polarization in the central portion of the cylinder is being filled in by other nuclei diffusing into this section, rather than by thermal repolarization, which is what would happen in water, for example.



Two 1-D diffusion images of the ^3He gas. (a) A diffusion image with the gas at thermal equilibrium at room temperature. The diffusion coefficient away from the ends of the cylinder matches that measured earlier by a completely different diffusion-inflow method. The lowering of the diffusion coefficient near the walls of the cylinder is due to the walls restricting the diffusion in this area. (b) A diffusion image when the cylinder had a thermal gradient produced by holding the right-hand end of the cell in a liquid-nitrogen exhaust plume. For an ideal gas, the diffusion coefficient is proportional to the square root of the absolute temperature. The thermal gradient is nicely represented by the diffusion gradient in this image. Again, the lowering of the diffusion coefficient at the ends is due to restricted diffusion.

The Development of Fullerene-Based Hydrogen Storage Systems

Shimshon Gottesfeld

The objectives of our project are to evaluate hydrogen uptake of fullerene substrates and to probe the potential of the hydrogen/fullerene system for hydrogen fuel storage. We have made significant progress in demonstrating conditions for substantial and reversible hydrogen uptake/release by fullerenes. We have completed and tested a system for measuring hydrogen uptake that is capable of handling both a vacuum of 1×10^{-6} torr and pressures greater than 200 bars. Operation of the system is fully automated and controlled by computer.

We obtained the first promising results using fullerene-ruthenium samples prepared by reacting fullerenes with ruthenium carbonyl and then annealing the samples at

600°C under high vacuum to remove residual carbonyl groups. This form of modified fullerene was designed to provide effective hydrogenation catalysis as well as increased intermolecular gaps in solid fullerenes. We used a hydrogen pressure cycle (0 to 140 to 0 bars) to measure reversible hydrogen uptake/release by the fullerene-ruthenium sample at constant temperature. The threshold temperature for significant hydrogen uptake was somewhat over 200°C, and reversible uptake/release levels measured for the fullerene-ruthenium sample were 1.2% at 270°C and 2.0% at 350°C. Later, we discovered that an unmodified fullerene exhibits similar hydrogen uptake/release behavior under similar pressure-swing conditions when hydrogenation is catalyzed

by a platinum strip located above the fullerene sample. Reversible isothermal hydrogen uptake levels for the unmodified fullerene were 0.9% at 200°C, 1.4% at 300°C, and 2.6% at 400°C.

We suspect that hydrogenation proceeds by incipient sublimation of fullerenes, as indicated by our thermogravimetric analysis measurements. These results provide original, significant data on the extent and mechanism of hydrogen uptake/release by fullerenes and, consequently, on the viability of the hydrogen/fullerene system for hydrogen storage. Of particular interest is our demonstration of reversible uptake/release at levels exceeding 2% for isothermal-pressure-swing conditions. We hope to increase hydrogen uptake further by optimizing the composition and structure of the catalyzed fullerene sample.

Optical Imaging through Turbid Media Using a Degenerate, Four-Wave, Mixing Correlation Time Gate

Irving Bigio

There is a significant need for a safer alternative to x-ray imaging for applications such as mammography, dentistry, and brain imaging, and near-IR optical diagnostics could fit the bill. However, because tissue strongly scatters light, resulting in diffuse or fuzzy images, a method is needed for selecting and amplifying only the small number of photons that have traveled nearly unscattered through the tissue medium. Practically, this is equivalent to detecting only those photons that have taken the straightest (that is, the shortest temporal) path through the medium.

The goal of this project is to develop an optical imaging diagnostic based on the nonlinear optical

technique of degenerate four-wave mixing as a very fast correlation time gate. This method generates a short, well-defined optical gate for the imaging signal, which ensures that only the least-scattered photons are detected and imaged.

This year we designed and assembled a tunable near-IR laser (Cr:LiSAF) and explored the use of new nonlinear media, identifying a specific dye solution in toluene that improves the signal-to-noise ratios. In addition, we generated the first images of a crosshair test pattern, at wavelengths appropriate for imaging in tissue, through 2 cm of scattering medium. We improved the configuration of the optical system and refined

our component specifications to obtain excellent resolution of the crosshair images. Finally, we also began designing a cesium-vapor cell for the nonlinear medium, which we expect to provide several orders of magnitude further improvement in the signal-to-noise ratio.

Publications

Zerkle, D.K., I.J. Bigio, and N. Nogar, "Imaging through Turbid Media with a Nonlinear-Optical Correlation Time Gate," *OSA Trends in Optics and Photonics* 2, 103 (1996).

High-Average-Power, Intense Ion Beam for Materials Modification and Other Applications

Harold A. Davis

We are developing a 1- to 2-Hz repetitive, intense, ion-beam source for materials studies (see figure). Specifications call for a beam energy of 200–250 keV, a beam current of 10–15 kA, and a pulse length 1 ms. The beam will be produced in a magnetically insulated diode with an active plasma anode. Applications for the source include (1) materials surface treatment through rapid melt and resolidification, (2) coating at high rates through vaporization of targets and deposition onto substrates, (3) a diagnostic neutral beam for the next generation of tokamaks, and (4) an intense pulsed-neutron source for detecting land mines and producing medical isotopes.

The major accomplishments this past year have been in the area of designing and fabricating the ion-beam system. We have designed a layout of components for the high-voltage modulator, sized the overall beam and power supply system, and completed design of the diode and vacuum system (including the anode-plasma generation system, the vacuum interface, the diode vacuum chamber, the beam transport and materials processing chamber, and the vacuum pumps, valve mounting, and plasma diagnostic vacuum chamber). Fabrication of these parts is under way. The first attempt to encapsulate the active plasma, high-voltage coil was unsuccessful, requiring a redesign; fabrication on this part is out for bid now. We also built and tested the plasma-anode and puff-valve drive circuits.

In addition, we have successfully modeled the thermal transport in the plasma coil with a finite-element code and determined cooling requirements for the anode-plasma induction coil. We have modeled and optimized the

accelerator and fast-coil circuits, and we have also modeled the plasma formation and acceleration process with a snowplow model (i.e., coupled-circuit and momentum equations).

Publications

Davis, H.A., et al., "Intense Ion Beam Treatment of Materials," *Bull. Mater. Res. Soc.* **21** (8), 58–62 (1996).

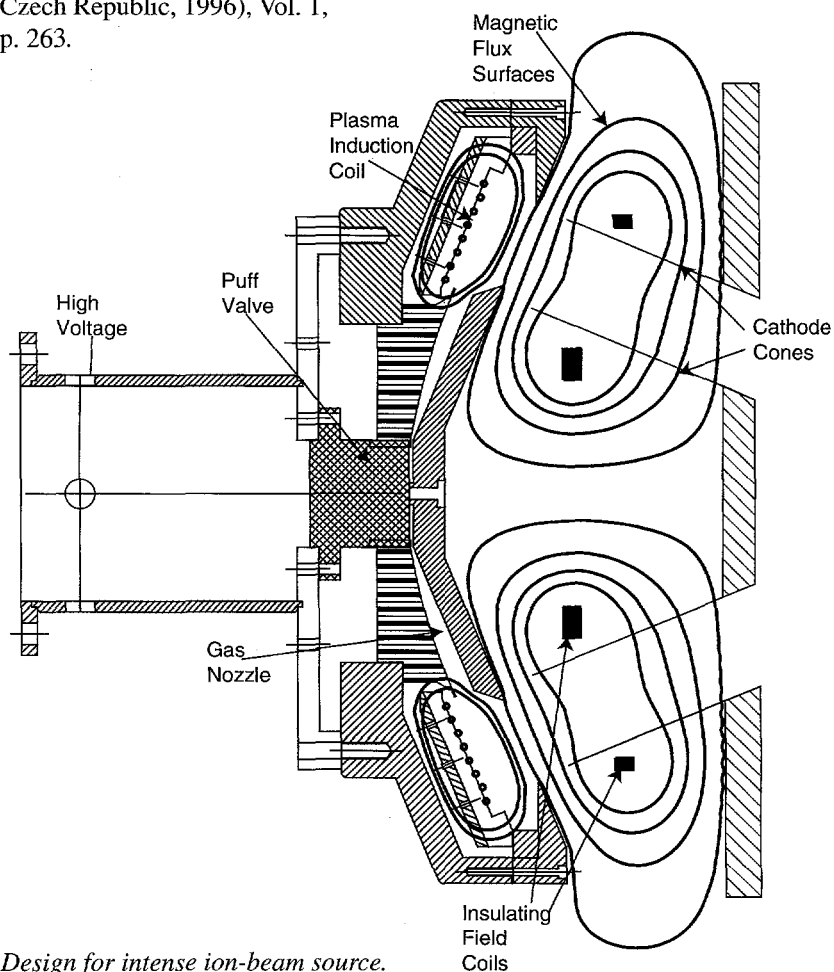
Davis, H.A., et al., "Progress Toward a Microsecond Duration, Repetitively Pulsed, Intense Ion Beam," in *Proc. 11th Int. Conf. High Power Particle Beam* (Tiskárna, K., Ltd, Prague, Czech Republic, 1996), Vol. 1, p. 263.

Davis, H.A., et al., "Progress Toward a Microsecond Duration, Repetitive, Intense Ion Beam for Active Spectroscopic Measurements on ITER," *Rev. Sci. Instrum.* **68**, 332–335 (1997).

Jiang, W., et al., "Thermal Imaging Experiments on the Anaconda Ion Beam Generator," in *Proc. 11th Int. Conf. High Power Particle Beam* (Tiskárna, K., Ltd, Prague, Czech Republic, 1996), Vol. 2, p. 890.

Rej, D.J., et al., "Materials Processing with Intense Ion Beams" (to be published in *J. Vac. Sci. Technol.*).

Rej, D.J., et al., "Materials Processing with Intense Pulsed Ion Beams" (submitted to *J. Vac. Sci. Technol.*).



Design for intense ion-beam source.

Rej, D.J., et al., "Preparation of Diamond-like Carbon and Boron Nitride Films by High-Intensity Pulsed Ion Beam Deposition," in *Proc. 3rd Int. Conf. on Applications of Diamond Films and Related Materials*, A. Feldman et al., Eds. (National Institute of Standards and Technology, Gaithersburg, Md., 1995), p. 723.

Rej, D.J., et al., "Surface Modification of AISI-4620 Steel with Intense Pulsed Ion Beams" (to be published in *Nucl. Instrum. Methods Phys. Res. B*).

Yatsui, K., et al., "Preparation of Thin Films by Ablation with the Anaconda Ion Beam Generator," in *Proc. 11th Int. Conf. High Power Particle Beam* (Tiskárna, K., Ltd, Prague, Czech Republic, 1996), Vol. 2, p. 894.

Multichip Module Technology Development

Jon Kapustinsky

In this project we are exploring whether several instruments under development at Los Alamos could be miniaturized using new multichip module (MCM) technology for the electronics and instrument readout. To that end, we addressed the problems associated with getting dies of the required precision. We worked with a vendor and used a prototype PHENIX silicon preamplifier, analog memory,

analog-to-digital converter (ADC), and control chips to produce a small (approximately 5- to 10-die) MCM.

We successfully created specifications for the small MCM, designed it, and submitted it for fabrication. To accomplish this process we had to engage in significant amounts of communication and collaboration with the fabrication team, and we demonstrated that the Los Alamos

design tools can generate files that can be transferred to the MCM foundry as planned. Our Oak Ridge National Laboratory collaborators transferred technical information about the PHENIX preamplifier, analog memory, ADC, and control chips that we incorporated into the design. We procured bare die parts, and we also developed the conceptual design of bare die testing. We will take measurements of the completed multichip modules so that we can determine the accuracy to which those tests must be performed to ensure acceptable yields.

Magnetic Resonance Force Microscope Development

P. Chris Hammel

Our central objective is to build a tool applicable to a wide range of studies of technologically important systems, specifically layered magnetic and semiconductor systems. We have accomplished four important goals in our program to apply the emerging capabilities of the magnetic resonance force microscope (MRFM). We have (1) quantified the sensitivity and resolution of the MRFM in a published article; (2) applied the MRFM to ferromagnetic resonance (FMR) studies of microscopic ferromagnetic samples and thus opened up a new arena of study; (3) developed a new approach to MRFM that will enable the use of novel, high-performance

resonators (the subject of a patent application in preparation); and (4) developed new RF hardware especially appropriate for MRFM.

These last two advances are directly in support of our ongoing work with our California Institute of Technology collaborators on development of the next-generation high-performance microresonators and on incorporation of these resonators into the MRFM instrument. These accomplishments are crucial steps in our program to apply the emerging MRFM technology to important technological problems in interface science. Potential applications include buried interfaces in layered microelectronic and magnetoelectronic devices.

Publications

Hammel, P.C., Z. Zhang, et al., "Sub-Surface Imaging with the Magnetic Resonance Force Microscope," *J. Low Temp. Phys.* **101**, 59 (1995).

Zhang, Z., P.C. Hammel, and G.J. Moore, "Application of a Novel RF Coil Design to the Magnetic Resonance Force Microscope," *Rev. Sci. Instr.* **67**, 3307(1996).

Zhang, Z., P.C. Hammel, and P.E. Wigen, "Observation of Ferromagnetic Resonance in a Microscopic Sample Using Magnetic Resonance Force Microscopy," *Appl. Phys. Lett.* **68**, 2005 (1996).

Zhang, Z., M.L. Roukes, and P.C. Hammel, "Sensitivity and Spatial Resolution for Electron-Spin-Resonance Detection by Magnetic Resonance Force Microscopy," *J. Appl. Phys.* **80**, 6931-6938 (1996).

Femtosecond Scanning Tunneling Microscope

Antoinette Taylor

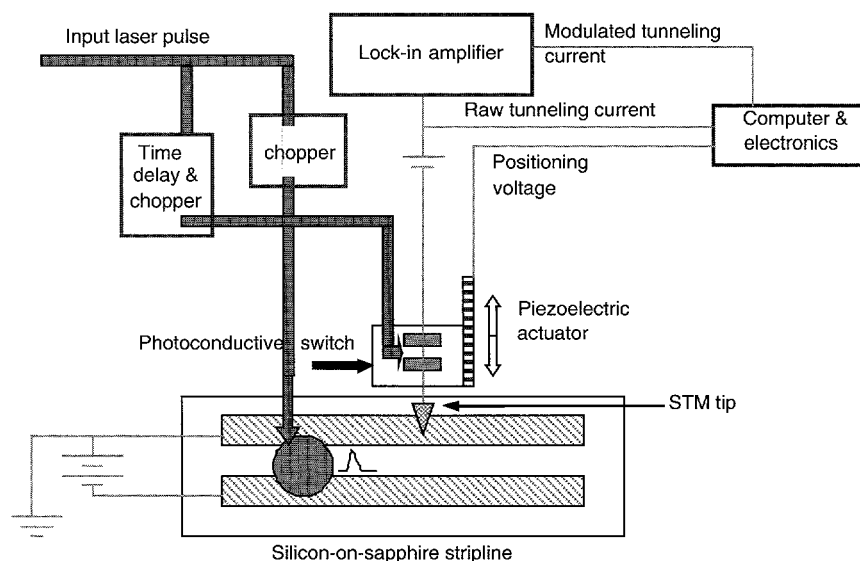
By combining scanning tunneling microscopy with ultrafast optical techniques, we are developing a novel tool to probe phenomena on atomic time-and-length scales. The goal of this project is to build the first femtosecond scanning tunneling microscope (STM). The <1 -ps temporal resolution of this STM will exploit the tip-sample nonlinearity. We will undertake research to characterize and understand the physics of the tip-sample interaction under transient conditions for a variety of sample materials to optimize the temporal resolution, sensitivity, and dynamic range this ultrafast STM.

We have assembled a custom STM and optical system that permits a wide range of flexibility to accommodate the task of developing and optimizing ultrafast tunneling microscopy. We have examined various methods for demonstrating ultrafast time resolution of tunneling currents:

- direct laser rectification of the femtosecond pulse,
- the application of an ultrafast bias using a novel near-field, biased, terahertz emitter, and
- the incorporation of a photoconductive switch in the STM circuit, as shown in the first figure.

The use of the photoconductive switch has produced the best transient data (see second figure). In this method one of the laser beams provides the time-gate for tunneling

signal by briefly illuminating the photoswitch, which is fabricated from radiation-damaged GaAs and has an "open" time on the order of 600 fs. We have obtained a time resolution of 2.5 ps with a few tens of picoamps of average transient tunneling current. Presently we are working to understand and optimize the technical aspects of this method.



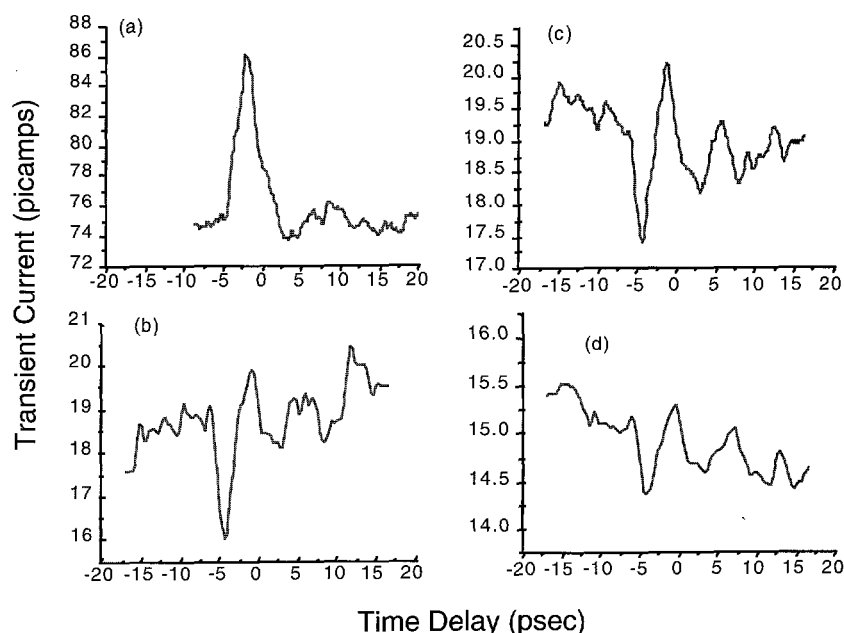
Femtosecond STM schematic: The feedback loop applies voltage to the STM piezoelectric actuator based on the raw tunneling current, in order to position the tip at a constant distance of a few angstroms from the metal stripline surface. The laser pulse train, consisting of 50-fs laser pulses at 100 MHz repetition rate, is split into two beams: one generates a subpicosecond electrical pulse which propagates down the stripline under the STM tip, and the other gates the STM measurement by briefly opening the radiation-damaged GaAs photoconductive switch. Lock-in detection occurs at the sum of the two chopping frequencies, thus indicating only that portion of the total tunneling current that is due to both the electrical transient on the stripline and the gating pulse. Scanning the time delay of the gating pulse with respect to the stripline excitation results in a time-resolved tunneling measurement.

Publications

Rodriguez, G., and A.J. Taylor, "Screening of the Bias Field from Terahertz Generation from Photoconductors," *Opt. Lett.* **21**, 1046 (1996).

Taylor, A.J., and G. Rodriguez, "Ultrafast Field Dynamics in GaAs Photoconductors" (submitted to *Appl. Phys. Lett.*).

Ultrafast tunneling signal, demonstrating picosecond resolution of the femtosecond STM: (a) Tip crashed into sample. (b) Tip weakly contacting sample (total resistance of GaAs switch and tunneling junction is 10 M Ω). (c) True tunneling with a total resistance of 16 M Ω . (d) True tunneling with total resistance of 33 M Ω . Note that the waveform of a true tunneling signal is the derivative of the signal obtained with the tip in contact with the sample (a).



Exploration of Technologies for Improving Civil Security

Eugene Farnum

Of the utmost importance to our security forces and to our government is the security of civilians, and new technologies for improving security are continually sought. Our project is aimed at increasing civilian protection by exploring the use of flexible-tile technology for bomb disposal containers, protective vests, and portable armor and then evaluating how the tiles, when combined with functional graded ceramics and ballistic modeling codes, can be used to improve security systems. After interviewing civil security forces, both state and Laboratory, to determine issues and needs, we reviewed the state of the art in security-system materials and contacted potential collaborators.

Work this year focused on the merits of using flexible tiles for improving bomb disposal containers, protective vests, and portable armor. During our investigation of bomb

disposal containers, two companies that were interested in having us evaluate their technologies fabricated such containers, which did not incorporate our flexible-tile technology, and delivered them to Los Alamos for testing. The companies' involvement was sponsored by the Industrial Partnership Office. Test results suggested that our flexible-tile technology would substantially improve explosive containment devices and led to a Los Alamos proposal to the National Institute of Justice for further technology development.

During our study of protective vests, we learned that Kevlar™ vests can be penetrated by ice picks. A collaboration with the New Mexico State Police established that our flexible-tile technology will significantly increase the protection offered by ballistic vests against ice picks and other pointed weapons without adding

undue weight and that it may be used by civilian police forces. Structural Laminates, a company with which we established a collaboration, donated some aluminum/fiberglass laminate that we used in experiments on Class IIa ballistic vests donated for testing by the New Mexico State Police. The tile-protected vests were successful in defeating hand thrusts with sharpened ice picks. We also designed an ice-pick test fixture capable of meeting the California Department of Corrections Penetration Standard.

Finally, for portable armor we designed an armored blanket that will provide portable protection of police vehicles from rifle fire. For the blanket, we acquired off-the-shelf ceramic/cermet tiles (similar to those previously used at Los Alamos in developing armor for the C-141 aircraft) and a bolt of appropriate Kevlar™ cloth, but lack of sufficient resources prevented us from completing and testing the blanket.

Fiber-Optic Communications Using Solitons (FOCUS)

Darryl D. Holm

The telecommunications industry is currently developing soliton-based optical-fiber networks in the hope of sending many scores of gigabits per second of digital data over fiber-optic links between computers and into homes and businesses. These soliton-based optical-fiber networks would use solitons (stable nonlinear optical pulses in nearly transparent fibers) as information bit carriers. Such networks would take advantage of the intrinsic stability of soliton solutions of the nonlinear Schrödinger equation, which to leading order describes the evolution of optical pulses in a lossless fiber. However, even in the highest-purity fibers, unavoidable energy losses cause soliton pulses to decay and disperse, thereby limiting data transmission rates. Reversing this dispersion, and thereby improving the rate of information transmission, requires devices that can reshape pulses. In this project we are designing and developing these devices theoretically and numerically by using and extending a general mathematical framework for analysis of nonlinear pulse transmission in optical-fiber networks.

This year we designed and analyzed a novel pulse recovery scheme using nonlinear optical loop mirrors. Because of the initial success of our results and the potential for their application in optical-fiber networks, the University of California decided to seek a patent on our pulse recovery scheme. We also invented a way of using nonlinear optical loop mirrors to generate high-quality soliton pulse trains. (Of course, a method of

reliably generating soliton pulses is a precondition for their use in optical transmission systems.) We have also developed a new perturbation technique for the study of optical-fiber amplifiers that should help guide future design developments and facilitate benchmarking of numerical simulation results. Next year we plan to continue our study of pulse-resaping devices and apply our perturbation technique to the development of numerical methods and algorithms for accurately computing soliton pulse propagation in optical fibers.

New Applications for Zeeman Interferometry

Roger Johnston

Our objective is to develop and explore new applications for the Zeeman Refractive Index (RI) Detector, which received an R&D 100 Award in 1992. The RI of a sample is the ratio of the speed of light in vacuum to the speed of light as it passes through the sample. Our instrument detects and measures changes as small as one part in a billion in the RI of a time-varying sample, such as a flowing gas or liquid. We developed the Zeeman RI Detector initially for monitoring air or gas samples for small changes in composition or contamination. Among the new applications for the technology explored in this project is a detector for gel electrophoresis, a detector for chromatography, and ultrasensitive thermooptic spectroscopy (a type of ultrasensitive spectrophotometry).

Publications

Cruz-Pacheco, G., and B.P. Luce, "The Relationship between Periodic Wavetrains and Solitary Waves in Optical Fiber Communications" (to be published in *Phys. Lett. A*).

Gabitov, I., D.D. Holm, and B.P. Luce, "Generation of Soliton Pulse Trains from Sinusoidally Modulated CW Beams with Nonlinear Amplifying Loop Mirrors" (to be published in *Opt. Lett.*).

Gabitov, I., D.D. Holm, and B.P. Luce, "Low-Noise Picosecond Soliton Transmission Using Concatenated Nonlinear Amplifying Loop Mirrors" (to be published in *J. Opt. Soc. Am. B*).

Gabitov, I., D.D. Holm, et al., "Recovery of Solitons with Nonlinear Amplifying Loop Mirrors," *Opt. Lett.* **20**, 2490 (1996).

This year we made significant progress in devising new applications for the technology, in making the instrumentation simpler, and in discovering new ways to use the instrument for ultrasensitive speciation. These new methods may ultimately prove to be patentable. Progress made during this project has led to two new cooperative research and development agreements (CRADAs), one of which is for pollution and process monitoring.

Publications

Johnston, R.G., "On the Matter of 'Ratioing'" (to be published in *Am. Stat.*).

A Comprehensive Monitoring System for Damage Identification and Location in Large Structural and Mechanical Systems

Charles R. Farrar

It would be very helpful if we could identify damage to large structures and mechanical systems at the earliest possible stage, before permanent damage to the structure or system, or injury to individuals, occurs. For this project we are developing and experimentally verifying a software package comprising state-of-the-art structural monitoring/damage-detection algorithms.

During the past two years of this research effort, we have reviewed the existing state-of-the-art methods of structural damage identification by measuring changes in the vibration characteristics of civil, mechanical, and aerospace structures; we also developed new algorithms that better detect damage. We are in the process

of assembling these algorithms into a interactive computer code.

This year we developed robust damage identification algorithms through numerical and experimental simulations. To quantify and locate damage using global vibration response measurements, we primarily looked at changes in strain energy stored in the structures; we determined the strain energy changes from changes in the mode shape curvature of the structures. We also developed and implemented statistical analysis methods whereby we can distinguish between changes in measured parameters caused by damage and those caused by random experimental error. This feature of our damage identification procedure is unique, and

it enhances our ability to detect damage in structures and mechanical systems.

Publications

Doebbling, S.W., and L.D. Peterson, "Computing Statically Complete Flexibility from Dynamically Measured Flexibility" (submitted to *J. Sound Vib.*).

Doebbling, S.W., L.D. Peterson, and K.F. Alvin, "Estimate of Reciprocal Residual Flexibility from Experimental Modal Data," *AIAA J.* **34**, 1678-1685 (1996).

Doebbling, S.W., L.D. Peterson, and K.F. Alvin, "Experimental Determination of Local Structural Stiffness by Disassembly of Measured Flexibility Matrices" (submitted to *J. Vib. and Acoustics*).

Farrar, C.R., "System Identification from Ambient Vibration Measurements on a Bridge" (submitted to *J. Sound Vib.*).

Quantum Cryptography for Secure Communications to Low-Earth-Orbit Satellites

Richard Hughes

Cryptanalysis techniques and algorithms are advancing rapidly and by the start of the twenty-first century will necessitate the development and use of new encryption technologies to ensure secure communications to satellites. The aim of our project is to develop quantum cryptography to provide absolutely secure encryption of communications to low-Earth-orbiting satellites. We will develop and demonstrate the cryptographic technology to a stage where it can be feasibly incorporated into new satellites.

Quantum cryptography uses single photons to create and transfer information in a way that utilizes the laws of quantum mechanics to afford absolute security. Our calculations show that with quantum cryptography, completely secure, random "seeds" (cryptographic keys) can be generated between a ground station and satellite in real time. By eliminating any prior record of a key, quantum cryptography removes the possibility of hostile interception of communications, making the entire encryption process both simpler and more assured.

During the past year, we have designed, constructed, and tested a quantum cryptography system that creates and transmits—using single-photon transmissions—cryptographic random numbers between a sending-and-receiving instrument within our laboratory. The system is based on the propagation and detection of non-orthogonal polarization states of single photons in free space at a wavelength (771 nm) for which the atmosphere has a very low attenuation. We are now taking the steps required to preserve the intellectual property rights to this invention before publishing papers or making public presentations about our system and its performance.

Application of Intense Surface Discharge VUV Light Sources to Photoresist Ashing in Semiconductor Manufacturing

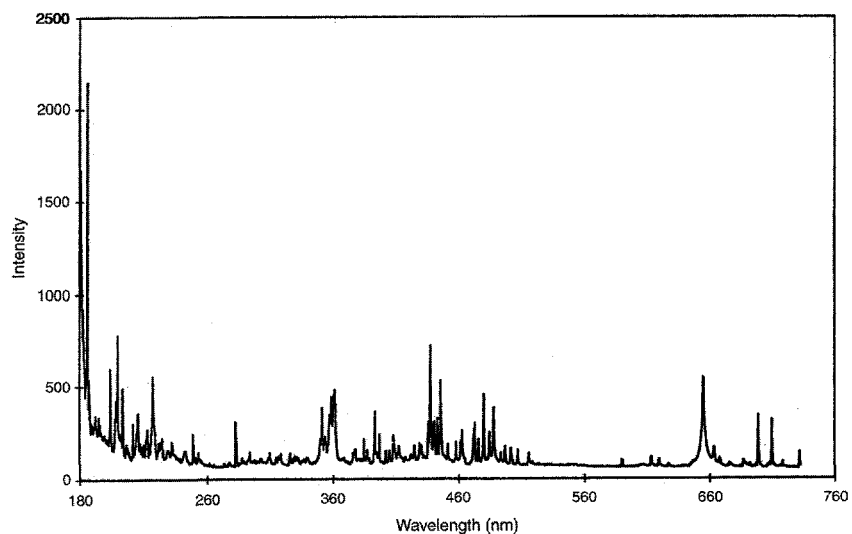
Robert Sze

This project deals with the development of a sliding-arc light source that would have sufficient intensity in the ultraviolet spectral region to do material processing over a very large area. The ability to melt thin-film materials in a single shot can have a major impact (for example, on the flat panel display industry) in such applications as the conversion of amorphous to polysilicon circuits on glass substrates used in liquid-crystal flat panel displays and in the activation of phosphors on electroluminescent flat panel displays.

The device we designed has a 6-in. $\times$ 6-in. discharge area on a dielectric surface for studies that have been made on alumina, teflon, and plate glass. At a charge voltage of 30 kV, the system stores some 2 kJ in pulse power. At this operating point we have shown a surface intensity uniformity of better than 5% across the entire surface area of the light flash. Integrated light-energy outputs on the surface from 200 nm to the infrared have been measured at greater than 800 mJ/cm². Preliminary attempts to crystallize amorphous silicon were unsuccessful, but crystallization was attempted at distances very far from the flash surface.

This year we focused our experimental efforts toward obtaining detailed light spectra of the flash. We have obtained instrumental distortion-corrected spectra from 160 to 735 nm

in helium, neon, argon, and krypton, as well as typical KrF and ArF excimer-laser gas mixtures and fluorine-containing gas mixtures in attempts to maximize uv production in these sliding-arc discharges. The first accompanying figure gives an example of such a study in argon. The second figure gives a comparison in the 160- to 360-nm UV range for argon and krypton. Krypton shows higher UV content, although the rising slope in UV light from black-body radiation is judged similar in both gases. The third figure shows that energy deposition into the discharge is greatly enhanced with increasing pressure as a result of increasing discharge impedance.



Flash spectra in 1000-torr argon gas on alumina dielectric from 160 to 735 nm.

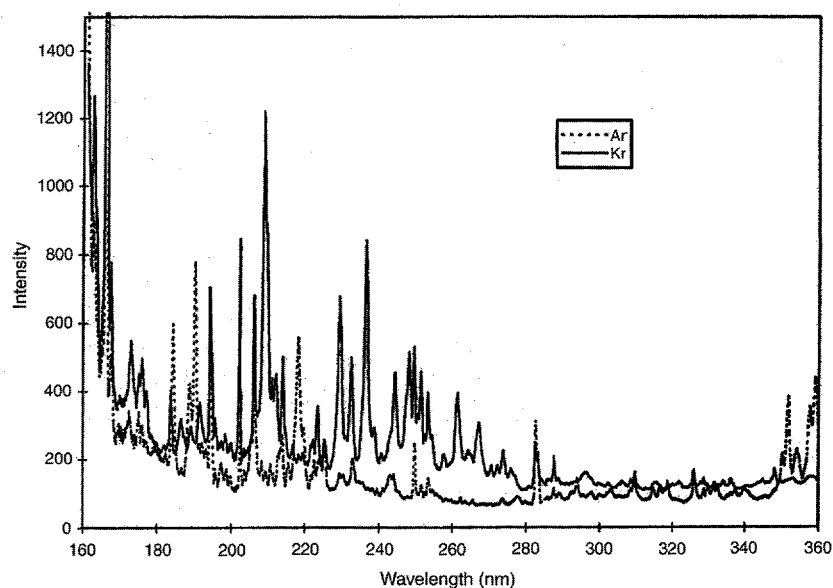
Publications

Hatanaka, H., and R.C. Sze, "Development of an Intense Surface Discharge Pumped Vacuum Ultraviolet Lamp" (Tenth IEEE Electron Devices Pulse Power Conference, Albuquerque, N. Mex., July 1995).

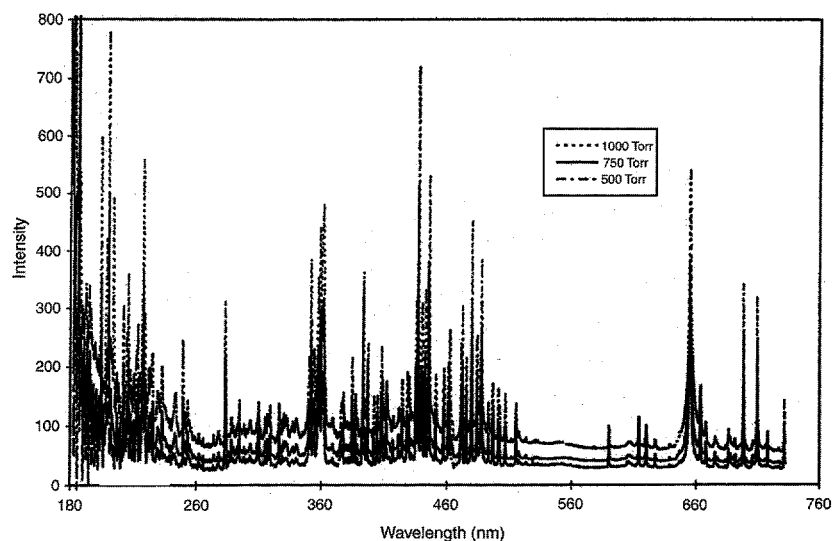
Sze, R.C., "Intense UV Light Source for Semiconductor and Flat Panel Display Processing" (Conference on Lasers and Electrooptics, Baltimore, Md., May 1995).

Sze, R.C., "Large-Area Surface Discharge UV Light Source for Materials Processing Applications" (to be presented at Gas and Chemical Lasers Conference, San Jose, Calif., February 17, 1997).

Flash spectra comparison at 1000-torr pressure between argon and krypton in the 160- to 360-nm UV range on alumina dielectric.



Flash spectra in argon at 500-, 750-, and 1000-torr pressure on alumina dielectric.



All-Solid-State Four-Color Laser

Timothy R. Gosnell

The goal of this project is to develop a solid-state laser that produces visible output wavelengths, including the commercially compelling blue wavelength. The device consists of a single-mode optical fiber doped with Pr^{3+} and Yb^{3+} ions. When the ions are simultaneously pumped with a near-infrared laser (860 nm), complex energy-transfer processes involving multiple excited ions lead to population of a high-lying energy level of Pr^{3+} .

Our main accomplishment this year was to verify and quantify the nature of the energy-transfer processes, in particular a "photon avalanche" process, responsible for the efficient population of the upper laser level. These results will be used to design a new geometry for the optical fiber, which was initially unoptimized, in order to enhance device performance.

Material Processing for Self-Assembling Machine Systems

Klaus Lackner

We are developing the foundation for a new technology based on self-reproducing machine systems. Of the numerous issues that need to be considered and resolved before our vision of the new technology can be implemented, material extraction is one, and it is the focus of our project. Limitations in energy and nonrenewable resources and the need to control deleterious side effects of human activities on the environment are major problems for the coming decades. Self-reproducing machine systems could be their solution.

Machine systems that build and maintain themselves promise an increase in industrial productivity as dramatic as that of the industrial revolution. A system that can build itself must procure all raw materials from its natural surroundings. Thus, next to automation, one of the most

critical issues in developing the new technology is the design of a process that will extract all the important chemical elements from raw dirt. This process differs from conventional extraction metallurgy in that it uses only abundant elements, because almost the entire mass of the self-replicating system is channeled through the process. However, such extraction processes are of interest even to conventional metallurgy because they do not involve use of expensive and sometimes hazardous materials.

This year, we have successfully collected a set of sample materials—for example, basalts—that are typical for the basic extraction process. However, most of our work to date has been performed on pure oxides and minerals. Because our new extraction processes occur at high

temperatures, we have been designing and building special, small, low-cost furnaces. We have reduced iron oxides and pure iron silicates with metallic silicon at 1600°C in air. Avoiding the need for a protective atmosphere is a major achievement because it greatly simplifies the ultimate design of the extraction process for self-replicating machines. We succeeded in extracting small iron pellets from raw materials. At the same time, our experimental results point to the need for a careful choice of the material for the containment vessel, which tends to be attacked by the melted charge. We have tested a number of materials and are optimizing our choice. *Discover* magazine (October 1995) referred to our concept as one of seven ideas that could change the world.

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Diode Laser Development for Quantum Computation

Richard Hughes

Quantum computation is much more powerful than classical computation because it allows computing with quantum-mechanical superpositions of many numbers at once. In a quantum computer, binary numbers will be represented by quantum-mechanical states ("qubits"). We have been developing a quantum computational device in which the qubits will be two electronic states of calcium ions that have been cooled with a laser to rest at a particular location in the ion trap. We will then perform quantum logical operations with a laser beam that is resonant with the qubit transition frequency and is directed at individual ions. Titanium-sapphire lasers are a proven

technology for this application, but they are expensive, require a laser expert, use over 40 kW of power, and fill an entire laser table. The objective of our project is to develop diode lasers for this application because they are easy to use, low in cost, and compact.

This year, we have developed diode lasers at the 866-nm and 794-nm wavelengths that are required for cooling calcium ions. (In the next few months, we will double the frequency of the 794-nm light to obtain 397-nm light.) We have assembled external-cavity diode laser systems and, with a prototype, demonstrated locking to an existing frequency standard. We have developed

frequency-offset techniques using modulators and/or ultrastable cavities to reference the 866-nm and 397-nm wavelengths to stable atomic lines. Typically, the wavelength of the light emitted by the laser must be controlled with respect to a reference wavelength, which is near to the desired wavelength. For our diode lasers, we can reference light wavelengths to an absolute atomic standard or to a very stable optical cavity that resonates at a very well defined frequency.

At the same time, we have worked with two companies to determine if the frequency-doubling cavities that they market would give the necessary amount of output power and would provide adequate beam quality for our 397-nm wavelength requirements. Finally, we have studied the Drever-Hall stabilization technique for external-cavity lasers as a means for producing laser linewidths of better than 100 kHz.

Designing a Micromechanical Transistor

Ronnie Mainieri

Micromechanical electronic systems are chips with moving parts. They are fabricated using the same techniques for manufacturing electronic chips, sharing their low cost. Micromechanical chips can also contain electronic components. The combination of mechanical parts and electronic parts makes it possible for chips to process signals mechanically. To achieve designs comparable with those obtained with electronic components, it is necessary for these

chips to have a mechanical device, i.e., a mechanical transistor, that can change its behavior in response to a small input.

Large responses caused by small changes are the hallmark of chaotic dynamics so most of the transistor designs we have considered correspond to chaotic systems. The chaos is in the ray dynamics of sound propagation. When we tried to compute the resonances of systems with chaotic ray dynamics, we

discovered that the numerically computed resonances had errors that grew exponentially fast with the resonance number. The errors also follow a universal curve independent of the shape of the device. The errors in the resonances imply an error for the time evolution of the system and may also be present in other equations. This exponential growth in errors makes it impossible to use traditional numerical techniques, and we are now characterizing the problem and approaching its solution using methods developed for the study of nonlinear dynamical systems. The basic idea is to combine Monte Carlo data with analytic methods.

High-Sensitivity, Solid-State Carbon Monoxide Sensor Development

Fernando Garzon

Carbon monoxide gas (CO) is a deadly, colorless, odorless gas that results from incomplete combustion of typical fuels. It is the most common form of death due to asphyxiant gases in the United States. Better

sensor technologies for this gas are needed to protect people in their workplaces and homes. Our objective is to develop simple, low-cost, electrochemical sensors for the detection of CO in air with tens of

parts per million sensitivities, good selectivity, and fast response times. The current commercial sensor technologies cannot detect carbon monoxide below dangerous threshold levels—tens of parts per million—nor do they respond quickly at the hundreds of parts per million levels.

We have produced, tested, and optimized solid-state electrochemical sensors that use thin-film perovskite- or fluorite-structure catalysts as sensing electrodes deposited on oxygen-ion, conducting solid electrolytes for monitoring carbon monoxide in air. Our sensors show excellent sensitivity: the ability to detect less than 1 ppm CO, rapid response time, and good return to baseline characteristics. They also show good long-term durability—over 1000 hours of operation under a variety of conditions.

We have studied the cross sensitivity of these sensors to carbon dioxide, water vapor, propane, methane, ethanol, and hydrogen. We have also demonstrated that variants of this technology can be used to sense other gases, such as hydrocarbons, sulfur dioxide, and nitric oxides. Our technology may replace semiconductor-based sensors currently in use because of the new devices' superior response characteristics. We have filed a patent application for this invention.

Acoustic Resonance Spectroscopy

Randy S. Roberts

US government agencies have successfully applied Acoustic Resonance Spectroscopy (ARS) to the problem of noninvasive classification of chemical munitions. The classification technique compares templates formed from the acoustic signature of known munitions to acoustic signatures of unknown munitions. One problem with this approach is template construction—specifically, determining which combination of signatures yields the best template. The objective of this project was to develop a technique to determine the best set of signatures to construct a template.

We have developed an approach that appears to be a promising solution to this problem. The approach involves successively adding new signatures to the template and monitoring discrepancies between successive templates. At this point we are evaluating the technique on several data sets. Additional work on this project included reporting a liquid-solid discrimination algorithm and exploring the application of ARS to such areas as gas-bottle inspection and pit surveillance. We obtained promising results in the former application, and results are forthcoming in the latter.

Liquid-Metal, Focused-Ion-Beam Etch Sensitization and Related Data Transmission Processes

Bruce Lamartine

Ultrahigh-vacuum focused-ion-beam micromilling is a method of recording data permanently at very high density. The process can potentially be significantly improved by ion-beam sensitization to wet or dry anisotropic chemical etch reactions. The objective of this project is to explore the general phenomenon of ion-beam etch sensitization in several media—e.g., silicon (100), gallium arsenide, and tantalum oxide on tantalum—for optimal pixel or bit contrast and to search for optimal

media and transmission formats for rapid digital transfer. In addition, we intend to explore, in hardware, the feasibility of a charge-coupled-device data transfer scheme that can send data at video rates.

The ion-beam micromilling process, while already successful, can be enhanced by ion-beam sensitization to wet or dry anisotropic chemical etch reactions. Ion-beam sensitization differs from conventional lithography in that many levels of feature depth are potentially available

(depending on the local, spatial ion dose) and that no organic or inorganic resist is required. We developed these unique features sufficiently during the past year to file several patent actions on applying this process to the production of both digital and human-readable grayscale data on archival media such as silicon and other single crystals or amorphous coatings. Furthermore, we showed that several micromachined data media can be used for human-readable formats (either pictures or print): silicon (100) can be read by a phase-sensitive interference microscope, silicon (100) and silicon (111) can be read by a laser intensity feedback microscope, and tantalum oxide can be read by a conventional scanning-electron microscope.

Experimental Validation of Superconducting Quantum Interference Device Sensors

Robert Kraus

Along with Sandia National Laboratories (SNL) and the University of New Mexico, we have supported the collaborative development of two critical components for a hand-held, low-field magnetic sensor based on superconducting quantum interference device (SQUID) technology. The two components are a digital signal processing (DSP) algorithm for background noise rejection and a small, hand-held, dewar cooled by a cryocooler (supplied by SNL).

We reported the results of the DSP algorithm implementation at the 10th International Conference on Biomagnetism. Traditionally SQUIDS have been operated in magnetically shielded rooms, costing approximately \$500,000 or more, to reduce

background fields sufficiently that they will not overwhelm the dynamic range of the SQUID. We implemented this novel approach developed as part of this LDRD project in a prototype system that enables cancellation of more than 99% of the background magnetic field at the SQUID. We used the principle of superposition of magnetic fields.

Using state-of-the-art electronics and digital circuits, we anticipate being able to cancel at least 80 dB (99.99%) of the background signal. This level of background cancellation at the SQUID makes applications such as monitoring head trauma or cardiac function in the field a realistic prospect and one that we will develop.

The hand-held SQUID sensor system is nearing completion as of the writing of this report. The battery-powered cryogenic cooler has been procured by SNL and the last parts of the dewar are in fabrication. The dewar design uses a thick aluminum wall for eddy-current cancellation of all but low-frequency signals, reducing further the ambient background at the SQUID, while allowing most of the biomagnetic frequencies of interest through the wall to the SQUID sensor.

A second hand-held dewar has been designed using G-10 glass-epoxy composite that will allow the entire electromagnetic spectrum to pass through to the SQUID. The aluminum design will enable use of the prototype DSP background cancellation system, since it is less reliant on complete removal of the background. The composite dewar will require highly efficient background rejection.

Plasmas, Fluids, and Particle Beams

High-Power, High-Frequency, Annular-Beam Free-Electron Maser

Michael Fazio

Free-electron masers (FEMs) operating in the microwave regime have demonstrated both high beam-to-RF power extraction efficiencies (~30%) and high output power (~GWs). In addition, FEMs are potential candidates for driving advanced particle-beam accelerators at relatively high frequencies (greater than 10 GHz). However, current FEM technology does not lead to adequate phase stability for this application. Furthermore, high output power has been demonstrated only with FEMs driven by induction accelerators at higher voltage than practical for driving long accelerators. Such a high-power RF source would enable the construction of future linear colliders that are simply too expensive to build with existing technology.

The objectives of this project are to (1) demonstrate high output power (0.5 GW) at high frequency (17 GHz), using a high-current but relatively low-voltage electron beam, and

(2) demonstrate a phase-stability scheme in which the RF phase of the output power is not affected by small fluctuations in the electron beam voltage. We have derived theoretical phase-stability criteria and designed a high-power FEM using the axial FEM interaction that satisfied these phase-stability criteria.

Most recently we have concentrated on prototyping and fabricating components for a high-power experiment. Because of the uniqueness of this experiment, completely new diagnostic techniques and RF matching components are needed. In particular, we have designed and built an input coupler, a high-power load, a slow-wave structure, directional couplers, and high-power calorimeters. We are now assembling the high-power experiment.

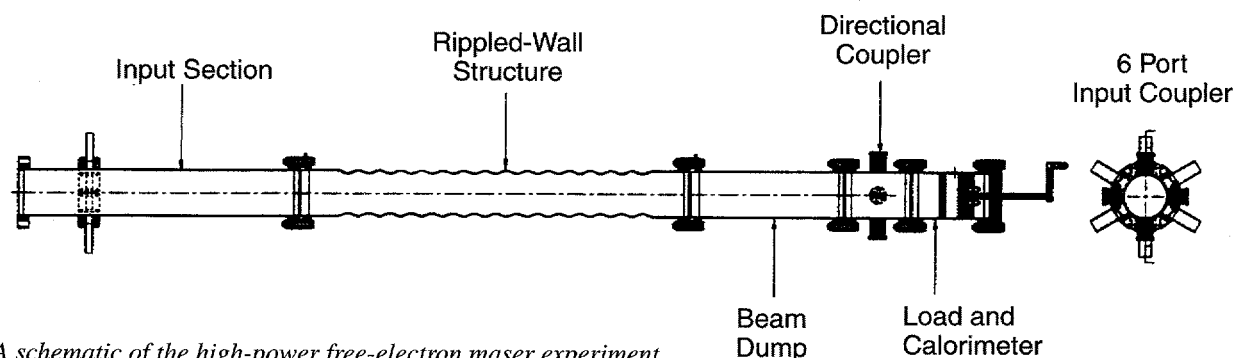
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Determination of Optical Field-Ionization Dynamics in Plasmas through Direct Measurement of the Optical-Phase Change

Antoinette Taylor

The interaction of ultrashort, high-intensity laser pulses with solid and gas targets is a field of growing interest. Highly ionized, atmospheric-density plasmas are a potential source of coherent visible-ultraviolet and x-ray light, as well as a potential medium for charged-particle acceleration. The interaction of a high-intensity, ultrashort pulse with a solid target is of interest both scientifically and as a source of ultrashort x-ray pulses.

New, quantitative experimental diagnostics compatible with ultrafast time scales are needed to measure the ionization and the subsequent plasma dynamics that give rise to these conditions. The goal of this project is to develop a technique for characterizing laser-plasma interactions with femtosecond resolution based on the direct measurement of the phase

change of an optical pulse. We can then use this technique to investigate femtosecond field-ionization dynamics in atomic and molecular gases and to study solid-target laser-plasma interactions.

This year, we developed this novel technique and used it to investigate femtosecond field-ionization dynamics in atmospheric-pressure noble gases. We focused an intense (10^{14} to 10^{16} W/cm²), ultrafast (100-fs) pulse into a cell containing a noble gas at a pressure of 1 atm or less; this pulse ionized the gas. We then measured the change in the optical phase and amplitude induced by the presence of free electrons in the ionized gas using the technique of frequency-resolved optical gating. With this setup we determined the evolution of the ionization dynamics in helium, neon,

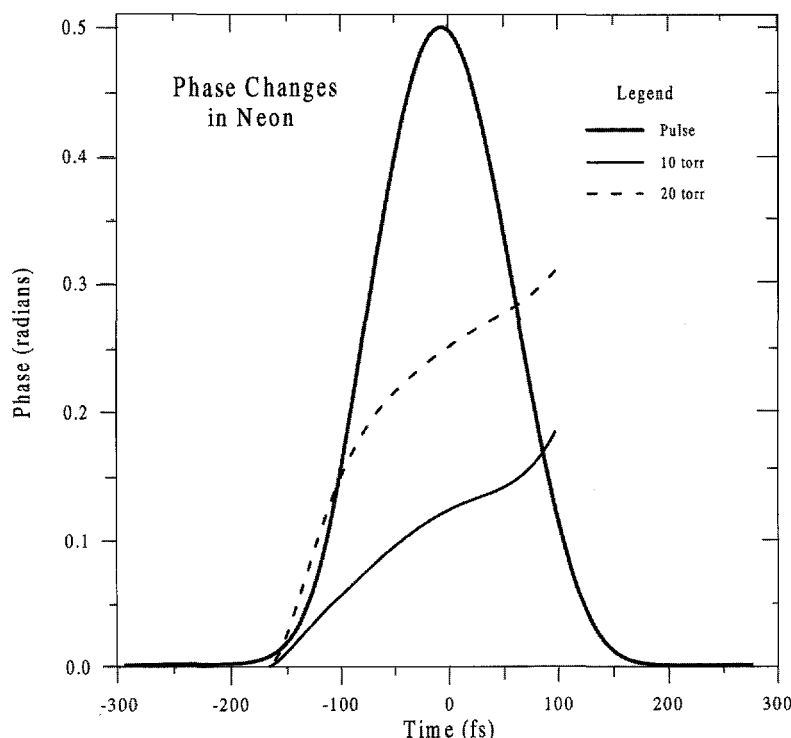
argon, krypton, and xenon as a function of pressure and pump intensity (see plot of phase vs time) and measured strong-field ionization rates of these gases. We modeled the ionization dynamics using strong-field tunneling theories—both Keldysh and Ammosov-Delone-Krainov (ADK)—and compared the results with our measurements (see plot of density vs time).

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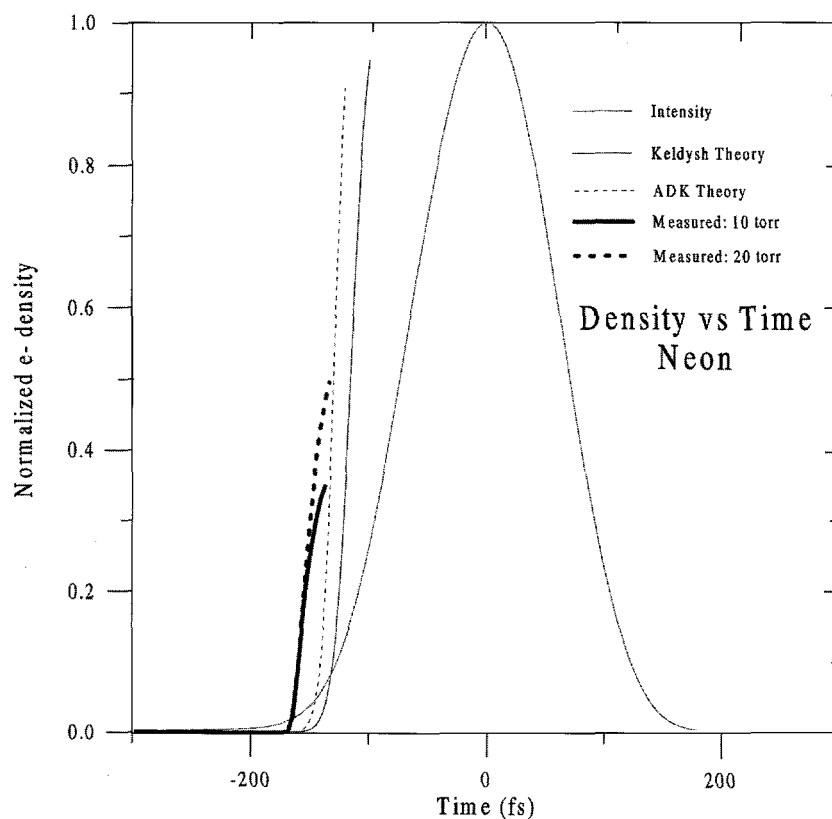
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Measurement of the phase change of the optical pulse due to the creation of the plasma in neon gas reveals that the magnitude of the effect scales with pressure, as expected. Consistent with theory, the onset of ionization occurs rapidly in the early stages of the pulse.

We analyzed the phase measurements from the other figure to yield the free-electron density as a function of time. The results are compared with calculations from both the Keldysh and ADK theories. The measured results demonstrate higher ionization rates earlier in the pulse than either of the theories suggests.



Delta-f and Hydrodynamic Methods for Semiconductor Transport

Lester E. Thode

The most sophisticated simulation technique for semiconductor carrier transport is the Monte Carlo method. Unfortunately, the Monte Carlo method is computationally costly. In this work we are investigating whether the delta-f method, developed within the magnetic fusion community, can be successfully applied to semiconductor transport. In addition, we are working to develop a single architecture to allow users to select fluidlike models, a Monte Carlo model, or a delta-f model.

Development of a C++ prototype plug-and-play code (PCUBED) is now complete. PCUBED allows the integration of different code languages within a single architecture, including C++, C, and FORTRAN

codes. PCUBED utilizes advanced input and output capabilities and includes interactive graphical debugging.

We imported the code MINIMOS into PCUBED to provide the drift-diffusion, energy-balance, and hydrodynamic models for the fluidlike part of the delta-f method. For the particle-tracking part of the delta-f method, we imported a new C++ object-oriented Monte Carlo code into PCUBED. We also developed new approaches to solve the nonlinear Poisson equation. To calculate moments of the distribution, we developed a general particle accumulation approach. To reduce noise, we are investigating higher-order particle-weighting schemes.

The plug-and-play nature of PCUBED has allowed use of the code in new areas such as neutron transport, brain tomography, and gas-core nuclear rocketry. Finally, we have shown that existing FORTRAN codes can be standardized with respect to input, output, restart, and graphics, which, if implemented, would lead to increased productivity of design efforts.

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A Compact Compton-Backscattering X-Ray Source for Mammography and Coronary Angiography

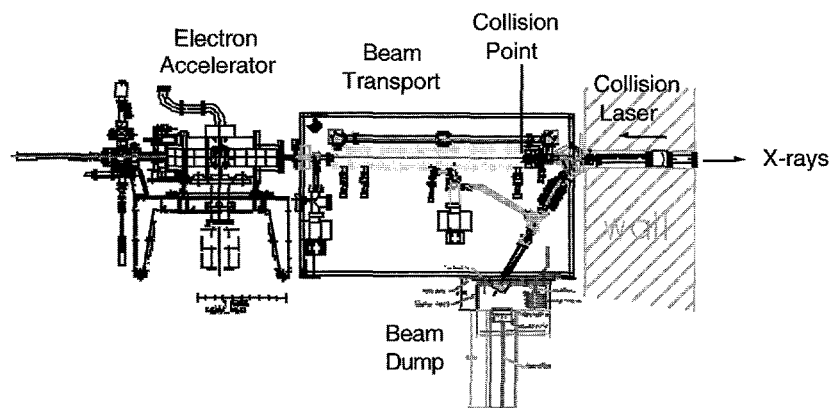
Dinh C. Nguyen

We are developing a compact, tunable, monochromatic x-ray source for applications in medical imaging such as mammography and coronary angiography. Using monochromatic x-rays in such applications will reduce the x-ray dose to patients and at the same time enhance the film image by reducing unwanted scatter. Our technical goal is to demonstrate the generation of a large flux of monochromatic x-rays in the keV energy range. We accomplish this goal by colliding a visible laser beam against a relativistic beam of electrons in a process known as Compton backscattering.

The experimental setup for Compton-backscattering x-ray generation includes a linear accelerator to produce the relativistic electron beam, a high-powered laser, and an optical resonator to trap the laser beam and to increase its intensity. For detecting the x-rays, we use a scintillator coupled to a light pipe that directs the visible fluorescence from the scintillator to a photomultiplier tube. These components are shown in the accompanying figure. In our experiments, the laser beam is used to generate electrons through a photo-emission process, and the trajectory of the electrons is timed so that they collide with the laser beam at a known position.

We have successfully tested the scintillation x-ray detector and found that it exhibits good sensitivity and good spatial discrimination against background radiation. We used a picosecond streak camera coupled to a charge-coupled device camera to overlap the electron beam and the laser beam in both space and time. Although the x-ray detector registered a positive reading, we could not conclusively demonstrate that the

signal arose from the Compton-backscattered x-rays because it did not completely go away when the laser was blocked. We are working on



The major components of the Compton-backscattering experiment.

several approaches to increase the yield of x-rays via Compton backscattering in order to meet our objectives.

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Equation of State of Dense Plasmas

John Benage

The goal of our project is to measure the equation of state of a dense aluminum plasma. We will accomplish this goal by using a laser to produce a shock in a uniform aluminum plasma plume. We will measure the velocity of the shock, the density in front of and behind the shock, and the temperature. From these measurements, we will determine the equation of state.

In the past year, we designed and completed the construction of the new capacitor bank which we will use to produce our plasma. The laser we will use to produce x-rays for the density measurements is operational, and we have begun tests on the production of these x-rays. We are just beginning

preliminary tests of the new capacitor bank; when these tests are completed, we will begin tests on the production of the aluminum plasma plume.

We also did a series of simulations of this experiment to determine the requirements for the laser that will be used to produce the shock in the plasma. These calculations showed that we need a 0.53- μm laser with a pulse width of 1–2 ns and an intensity at the plasma of 10 TW or greater. From these results, we designed a laser system which takes advantage of the system we already possess and, with a minimum cost, gives us the laser we need. We expect this laser to become operational by the middle of next year.

Turbulence and Turbulence Spectra in Complex Fluid Flows

Timothy Clark

Turbulence possesses a rich spectrum of time and length scales that defy direct computation because of the inability of foreseeable computers to resolve all scales. Turbulence strongly affects flows—e.g., mixing rates of pollutants, fuel in a combustor, or constituents in an inertial confinement fusion capsule. We are developing theoretical models of turbulence in parallel with direct numerical simulations of flows to produce tractable, accurate models for use in computer codes. We proceed from spectral models that describe turbulence in terms of a range of length scales. By exploiting emergent self-similarities of

the model predictions, we reduce these models to tractable approximations for engineering calculations.

This year we have developed a computer program to simulate inhomogeneous turbulence. We then used this program to isolate effects of triple- and pressure-velocity correlations from mean-flow effects. The resulting database is unique in the amount and quality of information regarding these correlations. We used this data to determine the necessity of maintaining certain tensorial and physical properties of the above correlations. Our simulations were uniquely appropriate to evaluate the

various models of the correlations. We have analyzed the self-similarity observed in spectral model calculations of a free-shear layer. Computations with more-advanced models of triple correlations yielded more-complicated and physically accurate self-similar forms; these results will assist us in improving engineering models. This is the most complete rigorous application of spectral theory to an inhomogeneous turbulence yet accomplished. The geometry is consistent with our simulations. The formulation employs an elegant methodology for specifying eigenstates for a wide variety of geometries.

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A Water-Filled, Radio-Frequency Accelerating Cavity

Rickey J. Faehl

The objective of this project is to study water-filled resonant cavities as a high-energy-density source to drive high-current accelerator configurations. Basic considerations lead to the expectation that a dielectric-filled cavity should be able to store up to ϵ/ϵ_0 (the ratio of the material to the vacuum dielectric constant), as much energy as a vacuum would with the same dimensions, and thus be capable of accelerating a proportionately larger amount of charge before cavity depletion occurs.

During this period, we confirmed that water-filled cavities with $\epsilon/\epsilon_0 = 60$ –80 did indeed behave with the expected characteristics, in terms of resonant TM modes and cavity Q. We accomplished this result with numerical cavity eigenvalue codes, with fully electromagnetic, two-dimensional, particle-in-cell codes, and most significantly with scaled experiments performed in water-filled aluminum cavities. The low-power experiments

showed excellent agreement with the numerical results. Simulations of the high-field, high-current mode of operation indicated that charged-particle loss on the dielectric windows, which separate the cavity from the beamline, must be carefully controlled to avoid significant distortion of the axial fields.

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A Target Plasma Experiment for Magnetized Target Fusion

Frederick Wysocki

Achieving controlled fusion is a scientific "grand challenge" that mankind has been pursuing for over 40 years. Fusion energy would help satisfy the long-term energy needs of the growing population on Earth. Magnetized target fusion (MTF) is an approach to controlled fusion in which a premagnetized, preheated target plasma is near-adiabatically compressed to fusion conditions. The objective of this project is to develop the ability to generate suitable target plasmas for MTF, the first critical milestone in the development path for achieving fusion with the MTF concept. Our approach involves driving a fast-rising electrical current reaching 1–2 MA through a fiber of cryogenically frozen deuterium about 200 μm in diameter. The fiber rapidly turns to plasma, heats, and expands to fill a plasma-containment chamber, thus becoming confined by the walls of the chamber. This project relies heavily on existing facilities and equipment at the Laboratory that are adapted to our needs.

This year, we designed and constructed a power-flow-channel and plasma-chamber system, and we incorporated this system into the Laboratory's Colt capacitor-bank facility. The capacitor bank has a maximum stored energy of 0.25 MJ, and it delivers a maximum of 3 MA of current with a rise time of 2–3 μs . We have performed initial plasma-formation experiments using a static fill of hydrogen gas. The diagnostics that we have fielded include an array of 12 B-dot probes used to determine

plasma current, a 1.3- μm laser interferometer to determine plasma density, an optical framing camera, a gated optical multichannel analyzer for visible spectroscopy, a visible to near-ultraviolet monochromator with time resolution for spectral time history, photodiodes to measure light emission, and the usual capacitor-bank monitors.

The data show that we are generating a plasma that lasts 10–20 μs with no obvious signs of impurities. Further analysis of the data is ongoing. The results from the 1.3- μm interferometer show that we need to go to a shorter-wavelength laser interferometer to reduce beam deflection caused by density gradients in the plasma and to reduce the overall sensitivity of the system. In accordance, we have borrowed a HeCd laser, purchased the supporting optics, and assembled and bench-tested the new interferometer. We will install the new interferometer on the actual plasma chamber in the upcoming weeks. We are also refurbishing the cryostat used for making the cryogenically frozen deuterium fibers and will be installing it on the plasma chamber in the next two months.

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Developing Electron-Beam Bunching Technology at Subpicosecond Pulse Lengths for Improving Photon Sources

Bruce Carlsten

The purpose of this project is to extend the current electron-bunch compression technology by developing a small experiment to study the essential physics associated with subpicosecond bunch compression, and to probe the fundamental limits associated with compression. In particular, our goal was to bunch 1 nC of charge to less than 1 ps, which would represent more than an order of magnitude increase in compression over previous experiments.

In previous years, we analyzed the dominant emittance growth mechanism and designed a second-order compressor. We also built a subpicosecond compressor on a new accelerator that was constructed for a plasma light-source. Using this compressor, we demonstrated compression of 0.1 nC from 20 to 0.25 ps and compression of 1.1 nC from 20 to 0.75 ps. These levels of compression far exceed previous results and provide important guidance to advanced compressor designs.

This year we used this compressed electron beam to generate as short as 22-nm-wavelength ultraviolet light, demonstrating tremendous improvement in an associated photon source. We analyzed additional compression effects in radio-frequency photoinjectors, and theoretically derived important formulas describing the nonlinear coherent synchrotron radiation force and the noninertial space-charge force that lead to emittance growth in compressor systems. Finally, we developed a new root-mean-square emittance diagnostic that can be used to study the emittance growth from these nonlinear effects.

Publications

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High-Intensity Laser-Matter Interaction Physics

James A. Cobble

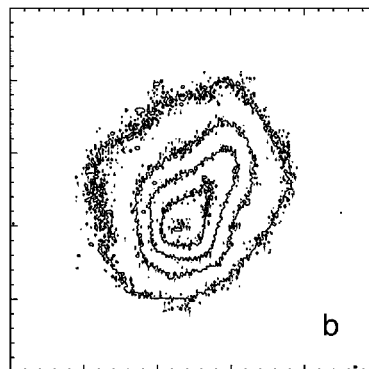
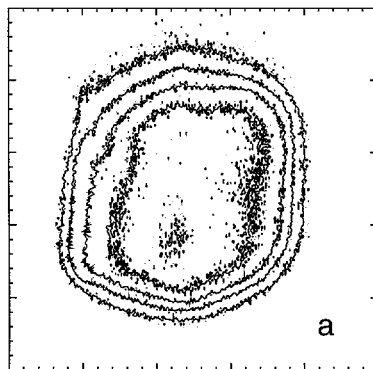
During the first year of research, we employed the short-pulse capability of the Trident laser at Los Alamos to measure the penetration of a high-intensity beam through a 1-mm scale length plasma. The highest laser irradiance was 7×10^{18} W/cm². The plasma density depends on the delay between a low-intensity plasma formation beam and the high-intensity probe in striking the plastic target. The critical plasma density is one above which the plasma oscillates quickly enough to reject the penetra-

tion of the light. Our experiment used plasmas of 1% to 5% of the critical density. The probe beam was focused with an f/2.5 parabola. We found that the beam f number increased upon passing through the plasma. It was more collimated because of its interaction with the plasma. In order to measure this effect, we allowed the transmitted beam to strike a diffuser plate behind the target. A camera imaged the scattered light from the plate to produce the data shown in the figure.

We also measured the reflected and transmitted light for different delays (plasma densities). Even at the low-plasma densities used, transmission was less than expected. There appears to be an anomalous absorption that is possibly related to the ultrahigh irradiance of the probe laser beam. We are pursuing this possibility with theoretical studies to model the behavior of the beam in the plasma. We are planning more experiments for the coming year.

Publications

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The f number of the probe beam is approximately doubled on passage through a 3% critical density plasma. The case with no plasma is shown in (a); the case with a plasma is shown in (b). Each frame is a 250 × 250 pixel array.

New Fullerene-Based Mixed Materials: Synthesis and Characterization

Duncan McBranch

Our goal is to develop novel composites of derivatized C_{60} (fullerene) in inorganic glass hosts. We seek to (1) understand the nonlinear optical properties of the fullerenes and (2) form optimized solid-state materials with properties that allow rapid change of optical transparency as a function of light intensity (for protection of eyes and sensors from harmful pulsed lasers).

We have formed glass composites containing C_{60} and soluble derivatives using our patented sol-gel techniques. We have demonstrated that the fullerene concentration in these glasses can be controlled over a wide range and that the resulting materials can be polished to high-quality surfaces and have optical damage thresholds much higher than those of plastic host materials.

We have observed enhanced optical limiting in solutions of a derivatized fullerene. Our transient absorption measurements determined the spectral and temporal regions of interest for optical limiting in C_{60} and derivatives and predicted enhanced limiting at longer wavelengths. Intensity-dependent transmission measurements confirmed these results. The increased solubility and broadened ground-state absorption of the functionalized C_{60} make it a more effective limiter in the red and near-IR spectral regions than the pure C_{60} (see accompanying figure).

We also used transient absorption to (1) determine the magnitudes of the excited-state cross sections as a function of wavelength and (2) demonstrate that the morphology of the fullerene molecules in the solid state

is a crucial parameter in the optical-limiting effectiveness for nanosecond pulses. Fullerene/sol-gel glasses are one of the most promising solid-state optical limiters in the near-IR spectral range.

Publications

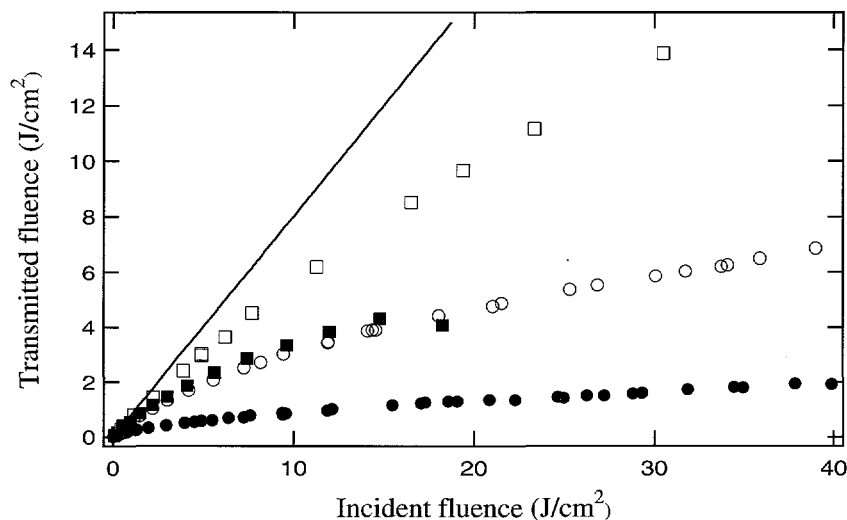
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Intensity-dependent transmission (T) for C_{60} at 532 nm (open squares, low-intensity transmission, $T = 80\%$) and 700 nm (solid squares, $T = 80\%$) and for the monosubstituted fullerene 6,6 phenyl- C_{61} -butyric cholesteryl acid at 700 nm (open circles, $T = 80\%$; solid circles, $T = 50\%$). The solid line indicates linear transmission of 80%.

Uses of Novel Selenium-Containing Chiral Derivatizing Agents: Potential Catalysis for the Chiral Oxidation of Simple Alkenes and Chiral-Promoted Aldol Reactions

Louis A. Silks

The last frontier for chemical catalysis is the design of chiral and environmentally benign chemical processes. Our goals are to develop (1) a new oxidative catalytic process to generate chiral allylic alcohols and (2) new chiral aldol reactions. We are using derivatives of selone reagents as chiral derivatizing agents (CDAs) for both goals. The arrangement of phenyl and methyl groups on these CDAs allows us to produce chiral products with predictable chirality from nonchiral starting materials.

Simple allylic chiral alcohols are precursors of many pharmaceuticals and agrochemicals. The successful synthesis of these alcohols would benefit chemical industry because the method would be catalytic, an easily recoverable co-oxidant could be used, and low levels of byproducts would be produced and, therefore, waste would be minimized. We successfully made the CDA adducts,

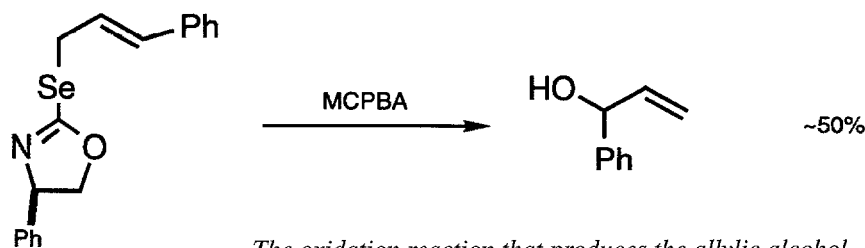
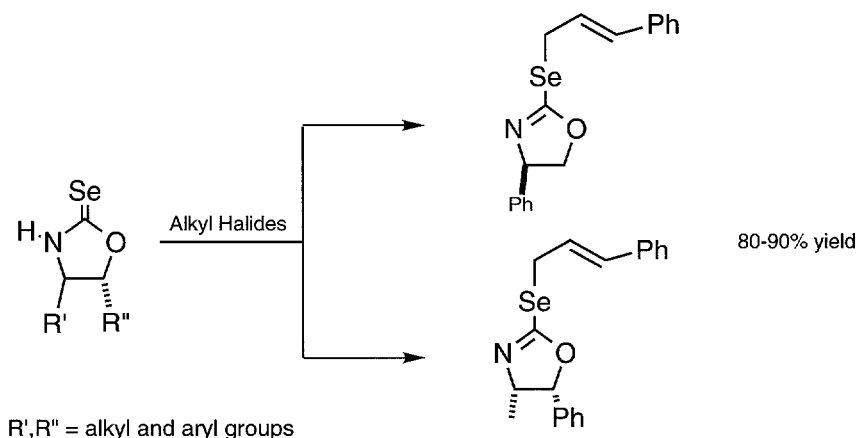
phenylglycinol- and norephedrine-derived selone, by reacting an allylic bromide with a chiral selone (see first set of reactions). We then oxidized these CDAs with *m*-chloroperbenzoic acid (MCPBA) to produce the allylic alcohol (see second reaction). Because the optical purity of the oxidation reaction was low, we are evaluating other oxidants and lower temperatures.

Chiral aldol reactions are another productive area for developing new methods for chiral inductions. For example, we can form two new chiral centers by enolizing an acylated selone with di-*n*-butylboron triflate (a Lewis acid) to generate an *E*-enolate that has boron chelated to both the oxygen anion and the selenium atom (see third set of reactions). We have

trapped the enolate with two different aldehydes. Although di-*n*-butylboron triflate is useful for generating the aldol product, the di-*n*-butylboron is difficult to remove from our desired product. To get around this problem, we replaced di-*n*-butylboron triflate with a boron-based Lewis acid that degrades in the presence of water.

More interesting is the use of titanium tetrachloride as the Lewis acid. From the proton nuclear-magnetic-resonance spectra, we know that the stereochemistry of the titanium-promoted aldol products differs from that of the boron-promoted products. This difference shows that we can reverse the product of the aldol reaction at the β -carbon atom by changing the acid component. In an effort to rigorously determine the stereochemical outcome of the reactions, we are currently attempting to grow crystals and obtain x-ray structures of our titanium- and boron-promoted aldol products.

Synthesis of the starting adducts of the selone CDAs from a chiral selone and an allylic bromide. The upper product (adduct) is a phenylglycinol-derived selone, and the lower product is a norephedrine-derived selone.

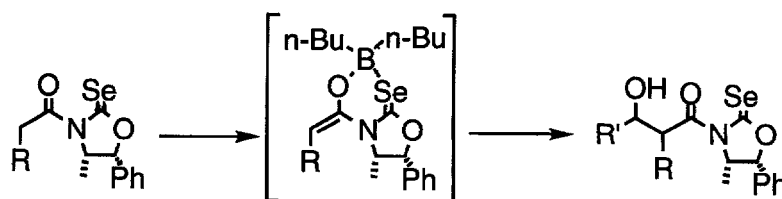


The oxidation reaction that produces the allylic alcohol.

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Wu, R., L.A. Silks, et al., "Highly Sensitive Spectroscopic Detection of Chiral Molecular Structures by ^{77}Se NMR Spectroscopy," *Spectroscopy* **11** (6), 37 (1996).

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R= methyl, O-benzyl

R'= alkyl, aryl

The aldol reaction that generates a product containing two new chiral centers. Di-n-butylboron triflate is the Lewis acid used.

Metal-Ligand "Multiple" Bonding: Revelations in the Electronic Structure of Complexes of High-Valent f-Elements

Carol Burns

Complexes of the f-elements containing multiply bonded functional groups (e.g., oxo, sulfido, imido, and phosphinidene groups) are important in actinide environmental science, waste management, and actinide materials chemistry research. For example, actinide hydrolysis yielding oxo- and hydroxide-containing species is important in dilute aqueous solution under certain pH conditions, and binary oxides and nitrides are important solid-state phases as both nuclear fuels and, in the case of oxides, as potential waste forms. Little is known, however, about the energetics and chemical behavior of these functional groups at actinide metal centers (important to the evaluation of the nature of interactions between f-metals and main group elements such as carbon, nitrogen, and oxygen). The goal of our project is to extend the development of the field of metal-ligand multiple bonding in coordination chemistry to include f-element analogs.

During the final year of this project, we have demonstrated important differences between the chemistry of the actinide elements and that of d-transition metals in bonding to main group elements. We have developed new multiple-electron-transfer synthetic pathways to prepare complexes with organoimido and oxo functional groups, which are unique to actinide elements. Theoretical studies suggest that f-orbitals may play a significant role in stabilizing multiply bonded functional groups. We have exploited these same multiple-electron-transfer pathways in examining coupling reactions of alkynes at actinide centers. Important differences exist between the reactivity of actinide and d-transition metal analogs, suggesting that organo-actinide complexes may have unique value in organic synthesis.

Publications

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Chemistry and Catalysis in Supercritical Media

William Tumas

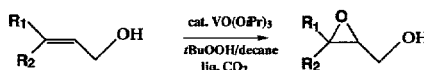
Our aim in this research is to explore the potential of supercritical fluids as reaction media for stoichiometric and catalytic chemical transformations in an effort to develop new, environmentally friendly methods for chemical synthesis or processing. This approach offers the possibility of opening up substantially different chemical pathways, increasing selectivity while enhancing reaction rates, facilitating downstream separations, and mitigating the need for hazardous solvents.

We investigated a number of catalytic processes for which carbon dioxide represents a viable solvent replacement. In several cases we have observed significant enhancements in selectivity and/or reactivity relative to conventional organic solvents. We have investigated the following catalytic processes: (1) selective oxidation including dihydroxylation and epoxidation, as shown in the first two figures, (2) asymmetric hydrogenation (see third figure) and hydrogen-transfer reduction (see fourth figure), (3) Lewis acid-catalyzed acylation and alkylation, and (4) coupling of amines with carbon dioxide to make isocyanates.

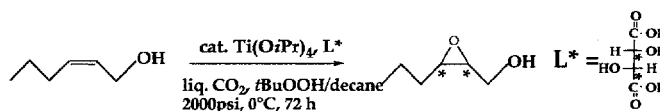
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Burk, M.J., S.G. Feng, M.F. Gross, et al., "Asymmetric Hydrogenation in Supercritical Carbon Dioxide," *J. Am. Chem. Soc.* **117**, 8277-8278 (1995).

Morgenstern, D.A., R.M. LeLacheur, D.K. Morita, et al., "Supercritical Carbon Dioxide as a Substitute Solvent for Chemical Synthesis and Catalysis," in *Green Chemistry*, P.T. Anastas, and T.C. Williamson, Eds. (American Chemical Society Symposium Series 626, Washington, D.C., 1996), pp. 132-151.

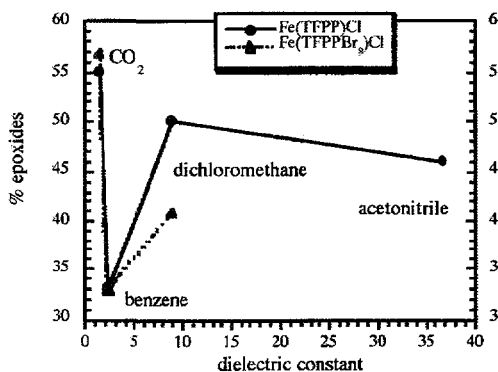
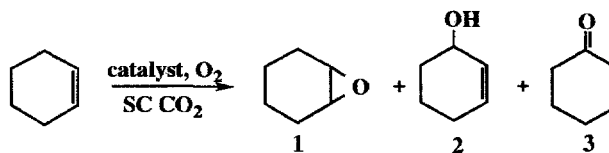


R ₁	R ₂	Time	T(°C)	Conversion	Products
CH ₃ -	H-	24h	25°C	>99%	$\text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_2\text{O}$ (85%) $\text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CHO}$ (15%)
nCH ₃ CH ₂ CH ₂ -	H-	24h	25°C	96%	$\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ (>99%)
CH ₃ -	CH ₃ -	24h	25°C	>96%	$\text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_2\text{O}$ (86%)
	CH ₃ -	24h	25°C	>99%	$\text{isopropenyl-CH}_2\text{O}$ (95%)
CH ₃ -		24h	25°C	>99%	$\text{isopropenyl-CH}_2\text{O}$ (>99%)



L*, R =	Conversion	Selectivity	% ee
(CH ₃) ₂ CH-	>99%	89%	87.4%

Selected results from the epoxidation catalysis: (top) vanadium-catalyzed epoxidation of prochiral allylic and homoallylic alcohols using VO(Oi-Pr)₃ and t-butylhydroperoxide; (bottom) enantioselective epoxidation of 2-hexenol using titanium catalysts containing chiral tartrate ligands.



Fluorinated iron porphyrin air-oxidation of cyclohexene: much higher selectivities to epoxide (cyclohexene oxide) are observed in supercritical carbon dioxide relative to conventional organic solvents.

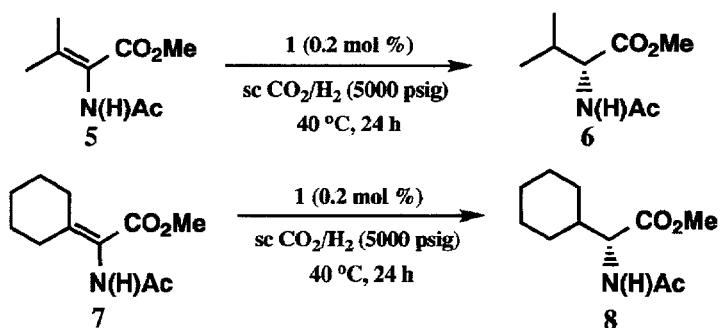
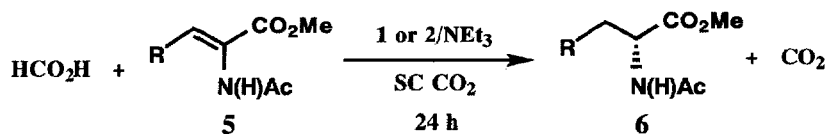
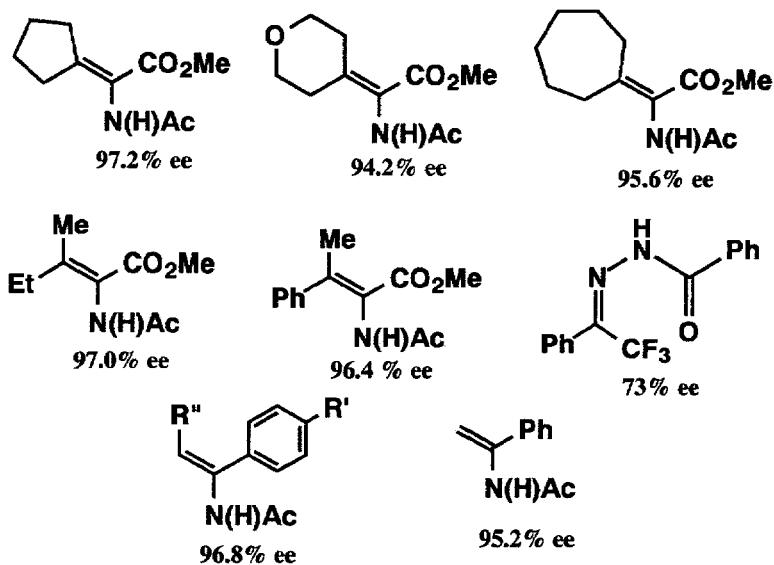


Table illustrates Rh-DuPhos enantioselective hydrogenation of enamides: higher enantioselectivity in supercritical carbon dioxide is observed for several substrates. Structures shown below the table illustrate the generality of high enantioselectivity for asymmetric hydrogenation in supercritical carbon dioxide.

Substrate	Catalyst	% ee		
		MeOH	hexane	Supercritical CO_2
5	1a	62.6	69.5	84.7
5	1b	67.4	70.4	88.4
7	1a	81.1	76.2	96.8
7	1b	95.0	91.2	92.5

Hydrogenation of β,β -disubstituted α -enamides with catalysts 1^a



Substrate	R	Temperature	% ee	
			Hexane	SC CO_2
5a	H	55	90.0	95.6
5a	H	35		96.5
5b	Ph	55	no reaction	88.5
5c	3,5-(CF_3) C_6H_3	55	no reaction	79.6
5d	Et	55	89.6	89.2

Asymmetric hydrogen transfer reduction of α -enamides using (r)-BINAP-ruthenium catalysts using formic acid/triethylamine.

Decay of Surface Nanostructures Via Long-Time-Scale Dynamics

Arthur Voter

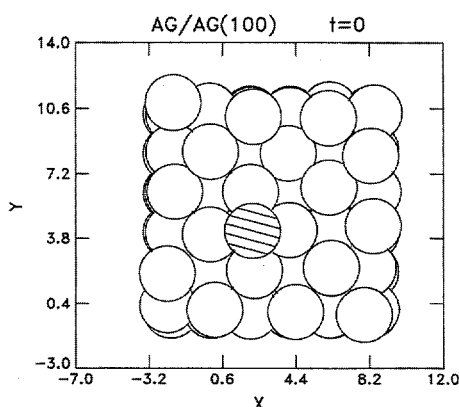
The main goal of this project is to develop a method for simulating infrequent molecular dynamics (MD) events even when the subsequent states of the system following the events are not known in advance. We have achieved a breakthrough this year and have in place a new working method. This method, which we term "hyper-MD," significantly extends the time period over which we can simulate classical molecular dynamics. To achieve this end, we augmented the true potential energy function with a bias potential that raises the energy in regions other than at the saddle points.

For strongly coupled, solid-state systems, we can construct such a bias potential from the local gradient and Hessian for the potential. An MD simulation performed on this modified potential allows transitions from basin to basin to occur at an accelerated pace, while the total time evolved becomes a statistical property of the system. This hyper-MD method should be most useful when the time scale of interest cannot be accessed with direct (or conventional) MD simulation, which is typically limited to a few nanoseconds, and when future events cannot be inferred from simple models.

We are presently testing the method by applying it to the diffusion of a silver atom on the Ag(100) surface.

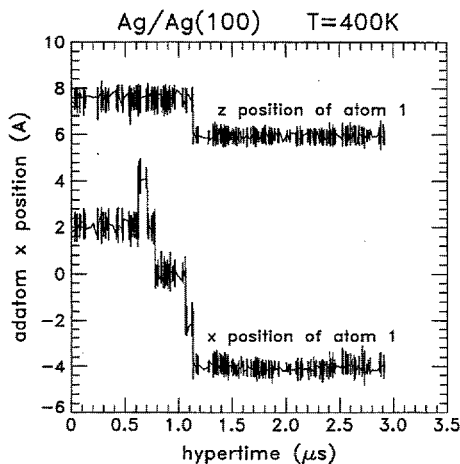
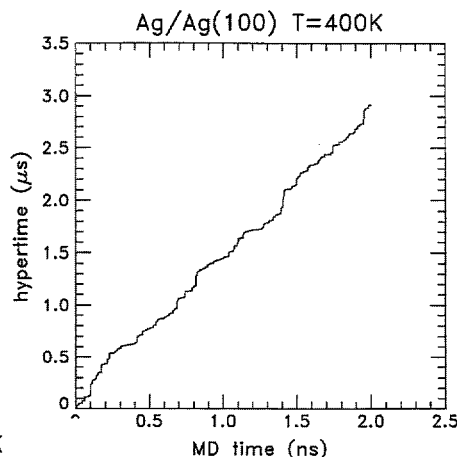
Time evolution of the x and z positions of atom 1, which is initially the adatom. After hopping for about 1.1 μ s, atom 1 exchanges with a top-layer substrate atom, which becomes the new adatom. For the remaining 1.9 μ s, atom 1 simply vibrates about its equilibrium position in the substrate.

Both adatom-hopping events and adatom substrate-exchange events occur at rates that are verified against exact calculations. The system is shown in the first figure. The evolution of the hypertime at $T = 400$ K is shown in the second figure, corresponding to a boost factor of 1500.



Surface-normal (z) view of the Ag/Ag(100) system. Atoms interact through an embedded-atom-method (EAM) potential. The system is periodic in the x and y directions. The top three layers are allowed to move during the dynamics, while two more-rigid layers below maintain the fcc(100) structure. The adatom is shaded for clarity.

Evolution of the calculated boosted time (or "hypertime") during the hyper-MD simulation. The system reaches 2.9 μ s after 2 ns of MD time, for a boost of about 1500. Because each hyper-MD step requires about 20 times more work than a simple MD step, the net computational gain is a factor of $1500/20 = 75$.



The initial adatom executes diffusive hops for about 1.1 μ s, at which time it exchanges with a substrate atom as shown in the third figure. This 2.9- μ s simulation took four days on a scalar workstation, but would require almost a year of computer time with direct MD.

Publications

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Solvation and Ionic Transport in Polymer Electrolyte Membranes

Thomas Zawodzinski

In this project we have studied the fundamentals of ion and solvent transport in polymer electrolyte membranes. Such membranes are a vital tool in separation and filtration processes that can be used in the nuclear complex, particularly in environmental aspects of those missions. In addition, these materials are of key importance in emerging battery and fuel-cell technologies. Our ability to radically change performance is greatly increased by gaining an understanding of these fundamentals.

We have begun calculations on model systems to develop two aspects needed for the final theory approach:

(1) good electronic structure calculations of appropriate models of the Nafion side-chain as one input for the theory, and (2) refinement of the dielectric continuum approach for the description of confined water layers. We carried out electronic structure calculations in trifluoromethane sulfonic acid (triflic acid), the anion (triflate), and several examples of clusters of a water molecule.

We also developed Monte Carlo methods to simulate water-oil-polymer mixtures. We expect that these techniques will allow us to construct physically reasonable models of hydrated Nafion membranes. Finally, we implemented

multigrid techniques in the dielectric solvation model to enable the study of the solvation of larger molecules.

We developed the needed techniques for the determination of the high-frequency (1–1000 GHz) dielectric response of ion-exchange polymers. Measurements on membranes of variable hydration state revealed features in the gigahertz range that are attributable to water relaxation. This is the first such result on a highly conducting system at such high frequencies. The electrophoretic nuclear-magnetic-resonance method will allow us to isolate the transport of individual ions in mixed ionic or mixed solvent systems, and thus obtain their mobilities and transfer numbers. We have recently built a new apparatus that allows us to study membranes. We also designed and constructed an electrochemical system with well-defined electrode processes for mobility measurements.

Heterogenization of Homogeneous Catalysts: The Effect of the Support

William Earl

The goal of our project is to covalently bind known solution (homogeneous) catalysts to the surfaces of high-surface-area, solid materials and to investigate the effects due to binding. We vary the structure of the solid surface and the chemical link between the catalyst and surface and measure the catalytic activity. This allows us to determine if there is a correlation between the final structure and catalytic activity. This project includes two phases of investigating heterogeneous catalysis. The first is to duplicate unusual data that already exists, as reported in the literature, and the second is to use similar compounds and syntheses to understand these results.

In the past year, we made progress in establishing the infrastructure and in synthesizing the starting materials required for the project. The first step was to synthesize the substrate to be used in the catalysis reactions. Although this was a relatively straightforward synthesis, the compounds were not commercially available and it was a multistep synthesis. The homogeneous catalyst used was fairly easy to synthesize. The difficult step in this work was modifying the homogeneous catalyst to allow linking it to the surfaces. The preparation process reported in the literature did not work as presented. We also acquired several zeolites and made minor modifications to them to allow

linking the homogeneous catalysts to them. In addition, we started the process of synthesizing high-surface-area silica with controlled pores. We will use these synthesized silica instead of commercial silica. Eventually, the solid materials will be characterized using a number of different spectroscopic probes. During the past year, we began some of these techniques, but the samples are, as yet, only partially characterized.

We ran several homogeneous reactions before linking the catalyst to the surface, and we established the methods to measure catalytic activity. These methods are applicable to homogeneous solutions and will be modified as we proceed to supported catalysts. At present, we are unable to quantitatively reproduce the literature results.

Photoredox Reactions: Energy Storage and Halocarbon Degradation

William Woodruff

Our project had five objectives: (1) to characterize the structures and the structural dynamics of the singlet and triplet states of selected metal-metal bonded systems; (2) to characterize the postexcitation, intramolecular electron-transfer reactions of these complexes; (3) to investigate strongly adiabatic photo-oxidative addition reactions, including the addition of halocarbons to the electronically excited complexes and their hydrogen-evolving reactions; (4) to seek effective reductant systems that will function in catalytic cycles and regenerate the original, reduced dimer; and (5) to explore the chemistry of metals less expensive than iridium or platinum with regard to their potential for photochemical reactivity.

Our results include studies of tungsten and molybdenum clusters with potential multielectron excited-state redox reactivity, metal-metal bonded dimers sequestered in liquid-crystal environments, d^7 dimers with long-lived photocycles, and photochemically produced oxygen-fluorine systems. These results have been reported in three research articles.

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Reactivity at Metal Centers Bound to Water-Soluble Catalysts

Nancy Sauer

We are examining water-soluble polymers as supports for homogeneous catalysts. Our approach is to covalently attach the catalyst precursors to these soluble polymers. The resulting macromolecular materials will mitigate loss of precious metals by modifying the solubility of the homogeneous catalyst. This approach will permit more benign solvent to be used and potentially will engender unusual substrate selectivity in the catalytic systems. The initial focus of the project has been incorporation of phosphine ligand onto water-soluble polymers as ligands for catalytically active metals such as rhodium. We are exploring the rate and selectivity of these systems.

Our work this year has focused on the attachment of phosphine ligands to the polymers. To demonstrate the reactivity of soluble supported metal centers, we have devised methods to prepare phosphine-functionalized polymers for incorporation of catalytically active metals into our soluble polymer systems. The work began with rhodium-phosphine hydrogenation catalysts that are active in aqueous solution. Accomplishments for this year include (1) preparation and screening of the baseline catalyst: $[Rh(NBD)(PPh_3)_2]^+$ (NBD is Norbornadiene); (2) synthesis and characterization of the molecular system with the chelating diphosphine

2,3-bis(diphenylphosphino)maleicanhydride (L); (3) development of methodology for attaching the chelating ligand L to organic nucleophiles; (4) synthesis and characterization of the molecular system with ring-opened chelating diphosphines 2,3-bis(diphenylphosphino)maleic acid monoethyl ester (L2) and 2,3-bis(diphenylphosphino)maleic acid monoethylenediamine amide (L3); and (5) screening of hydrogenation activity and selectivity for rhodium complexes with the three phosphine ligands L, L2, and L3.

Cyclodextrin-Based Chemical Microsensors for Volatile Organic Compounds (VOCs)

DeQuan Li

The goal of this project is to construct thin films of well-controlled, assembled nanotubes as novel sensing materials for chemical microsensor applications. These nanotubes provide a well-defined, hydrophilic porosity suitable for detecting small VOCs (such as benzene, toluene, chloroform, and trichloroethylene) that may contaminate water supplies. We can use our sensing materials for chemical separations and environmental cleanup, applications that are essential both for improving our health and safety and for saving money and resources. Our microsensor technology received an R&D 100 Award in 1995. The accompanying figure shows a schematic drawing of the sensor configuration.

To reach the targeted goals, we used modified cyclodextrins ("host compounds," so called because they are able to bind and surround smaller "guest" molecules) as the basic building units. We functionalized these building blocks with various organic groups, including linear alkyl chains and aromatic rings. These functional groups allow the cyclodextrins to self-assemble into tubular structures. We are currently in the process of purifying the building blocks that will self-assemble into nanotubes.

In another approach to constructing our thin films of nanotubes, we used charge interactions (the attraction of positive to negative charges) to assemble surface-receptors. We fabricated thin films from cyclodextrin

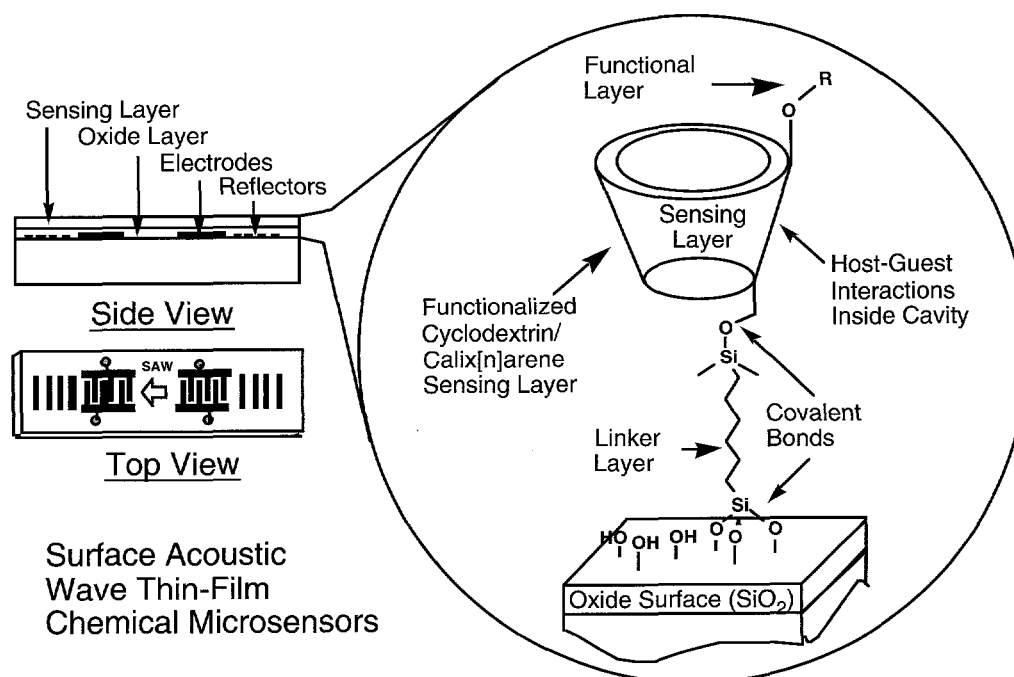
derivatives with charged functional groups and measured the sensors' responses to vapors containing known concentrations of VOCs. The results of these measurements indicate that it is feasible to construct sensor arrays to identify a wide variety of VOCs.

Publications

Li, D., J. Shi, et al., "Microsensors Based on Self-Assembled Cyclodextrin Host Thin Films for Volatile Organic Compounds" (Spectrum '96, Seattle, Wash., July 1996).

Swanson, B., and D. Li, "Cyclodextrin-Based Microsensors for Volatile Organic Compounds" (1996 American Chemical Society National Meeting, Orlando, Fla., August 1996).

Swanson, B., and D. Li, "Smart Film Sensor for Halogenated Hydrocarbons and Volatile Organic Compounds" (Incineration and Thermal Treatment Technologies, Savannah, Ga., May 1996).



Schematic illustration of a chemical microsensor based on surface-bound receptor molecules. This illustration shows an example of a cyclodextrin sensing layer on a surface acoustic device.

Binding of Hydrocarbons and Other Extremely Weak Ligands to Transition-Metal Complexes that Coordinate Hydrogen: Investigation of Cis-Interactions and Delocalized Bonding Involving Sigma Bonds

Gregory Kubas

At the forefront of chemistry are efforts to catalytically transform gas- or oil-derived hydrocarbons into useful products such as gasoline with metal compounds that chemically bind and break the inert carbon-hydrogen sigma bonds. Our first goal is to bind hydrocarbons, silanes, and germanes to metal complexes via their H-Y bonds (where Y is carbon, silicon, or germanium), analogous to our discovery of hydrogen (H_2) binding to metals. Studies of these unique "sigma complexes" ($M \cdots H-Y$, where M is a transition metal) will aid in developing new catalyst, sensor, and separation technologies. A second goal is to probe atom exchange between sigma-bonded molecules and other atoms bonded to the metal with techniques such as inelastic neutron scattering (INS). Such atom transfers, typically involving hydrogen, are the heart of catalysis, the lifeblood of the chemical industry and many biological processes.

We studied several transition-metal systems, including the molybdenum complex $Mo(CO)(PP)_2$, the manganese complex $[Mn(CO)(PP)_2]^+$, and the platinum complex $[PtH(PR_3)_2]^+$. In these complexes, PP is $Ph_2PC_2H_4PPh_2$ (where Ph is phenyl), and R is isopropyl. The platinum complex weakly binds the hydrogen-hydrogen bonds of H_2 and the carbon-chlorine or carbon-iodine bonds of halocarbons such as methylene chloride and iodobenzene (see first figure). The binding between the platinum and the carbon-hydrogen bonds is too weak to be observed.

In the molybdenum and manganese complexes, however, the metal interacts with intramolecular (internal) carbon-hydrogen bonds (see second figure). These carbon-hydrogen bonds are reversibly displaced by H_2 , N_2 , and silanes, which bind weakly to the positively charged manganese center. We have supported the manganese cation on alumina, and our calculations show that this material can be used to bind and separate hydrogen isotopes (H_2 , D_2 , and T_2) at room temperature rather than at the extremely low temperatures now used. This technology could be useful in tritium processing.

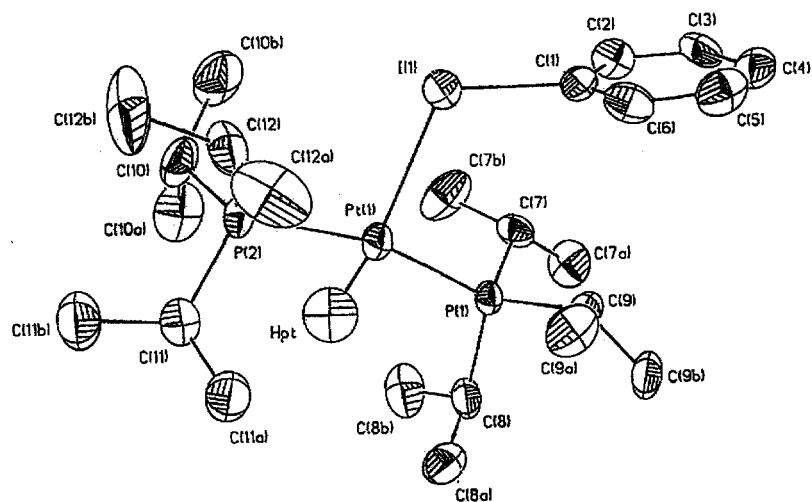
In the course of our study, we were able to prepare the first germane complex, $Mo(CO)(PP)_2(GeH_4)$, which relates to our discovery of the SiH_4 binding that models methane binding. We also studied H_2 rotation on

$[Mn(H_2)(CO)(PP)_2]^+$ and $RuH_2(H_2)_2[P(cyclohexyl)_3]_2$ by INS, which allowed us to probe atom exchange and interactions between hydride and H_2 .

Publications

Butts, M.D., G.J. Kubas, and J.C. Bryan, "Temperature-Dependent Behavior of Agostic Complexes $W(CO)_3(PR_3)_2$. Structures of Products of N_2 , Ethylene, and Silanes" (to be published in *Inorg. Chem.*).

Butts, M.D., B.L. Scott, and G.J. Kubas, "Synthesis and Structure of Alkyl and Aryl Halide Complexes of the Type $[(PiPr_3)PtH(\eta^1-XR)]BAR_f$ and Analogues with Et_2O , THF, and H_2 Ligands," *J. Am. Chem. Soc.* **118**, 11831 (1996).



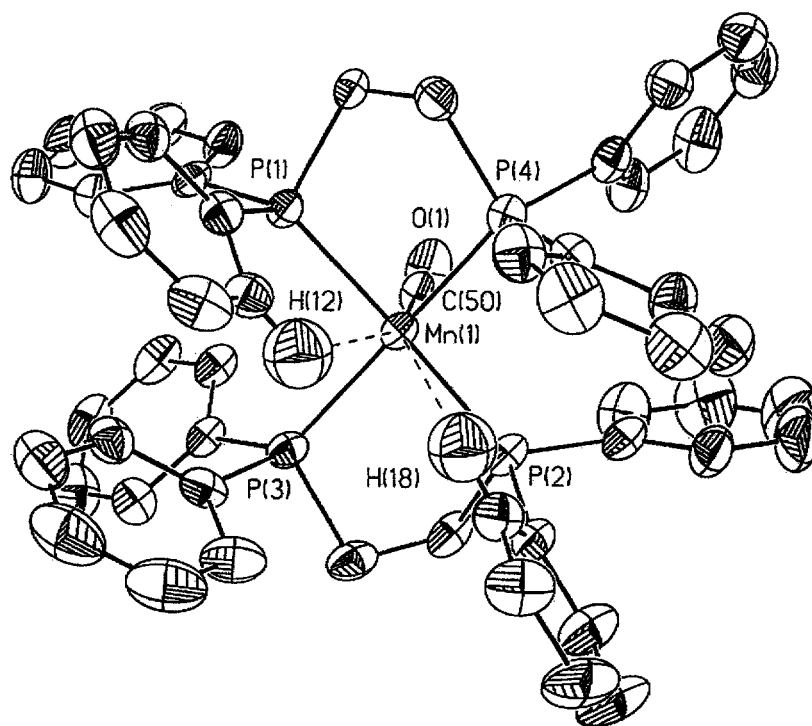
Molecular x-ray crystal structure of $[PtH(P-i-Pr_3)_2(PhI)]^+$ showing iodobenzene (PhI) binding to platinum. P-i- Pr_3 is tri-isopropylphosphine. This platinum complex is stable to air, a rare feature for such weak molecular binding but a feature that is highly desirable for sensor and separation technologies.

Eckert, J., A. Albinati, et al., "Nature of the Rh-H₂ Bond in a Dihydrogen Complex Stabilized Only by Nitrogen Bonds. Inelastic Neutron Scattering Study of TpRhH₂(η²-H₂) (Tp = Hydrotris(3,5-dimethylpyrazolyl)borate)," *Inorg. Chem.* **35**, 1292 (1996).

Kubas, G.J., "Metal-Silane Complexes" in *McGraw-Hill Yearbook of Science and Technology*, S.P. Parker, Ed. (McGraw-Hill Professional Book Group, New York, 1996), pp. 350-351.

Limbach, H.-H., S. Ulrich, S. Sabo-Etienne, et al., "NMR and INS Lineshapes of Transition Metal Hydrides in the Presence of Coherent and Incoherent Dihydrogen Exchange" (submitted to *J. Am. Chem. Soc.*).

Rodriguez, V., S. Sabo-Etienne, B. Chaudret, et al., "Spectroscopic Studies and Reactivity of the Bis-Dihydrogen Complex RuH₂(H₂)₂(PCy₃)₂ in Freons and CHCl₃. Synthesis of a Ruthenium IV Dihydride: RuH₂Cl₂(PCy₃)₂" (submitted to *Inorg. Chim. Acta*).



Molecular x-ray crystal structure of $[\text{Mn}(\text{CO})(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]^+$ showing the interaction (dotted lines) of the manganese(I) center with two carbon-hydrogen bonds located on separate phenyl (Ph) rings of the diphenylphosphine (PPh_2) groups. Multiple carbon-hydrogen interactions are rare. The analogous zero-valent molybdenum complex has only one such interaction.

Asymmetric Catalysis in Organic Synthesis

John Watkin

This research project is aimed at developing new catalysts for the enantioselective formation of organic molecules that may be used in a wide range of industrial applications. Our primary goal is to develop lanthanide-based catalyst systems that feature chiral alkoxide or Schiff-base supporting ligands.

During the past year, we have systematically examined the use of a wide range of lanthanide complexes containing chiral diolate and Schiff-base ligands as catalysts for the

asymmetric Meerwein-Ponndorf-Verley (MPV) reduction of acetophenone to a secondary alcohol. In one case, we have employed a Schiff-base ligand, prepared from norephedrine and 2-hydroxynaphthaldehyde, chelated to a gadolinium-metal center to perform the MPV reduction with an optical purity of 52%. Other lanthanide metals such as samarium, neodymium, and erbium were found to give somewhat lower optical purity in analogous reactions. The commercially available Jacobsen ligand used

in the same reaction gave better yields than the simple Schiff-base ligand, but the optical purities of the product were rather low, reaching a maximum of 38% in the case of erbium.

We have also examined the use of chiral diolate ligands chelated to a lanthanide-metal center for the MPV reduction. In this case, the yields were very good (>85%), but the optical purity was low (<20%), which we believe was due to the lack of rigidity in the diolate ligands. The results obtained to date have provided extensive information that will help us design more effective chiral ligands in the future.

Temperatures and Vibrational Frequencies of Liquid N₂/O₂ and CO/O₂ Mixtures Shock-Compressed to 10 GPa and 2000 K

Stephen C. Schmidt

The purpose of this project was to experimentally determine the temperatures and vibrational frequencies of N₂/O₂ and CO/O₂ mixtures that have been shock-compressed to pressures of ~10 GPa and temperatures of ~2000 K. The results obtained are used to improve the equation of state that describes mixtures at conditions characteristic of the expansion of explosive products. The measured molecular vibrational frequency shifts can be used to help develop molecular-potential functions that will allow calculations of thermodynamic equations of state.

We used a two-stage light-gas gun and single-pulse, multiplex, coherent anti-Stokes Raman scattering (CARS) to obtain vibrational spectra of carbon monoxide, nitrogen, and oxygen for several high-temperature, dense-fluid

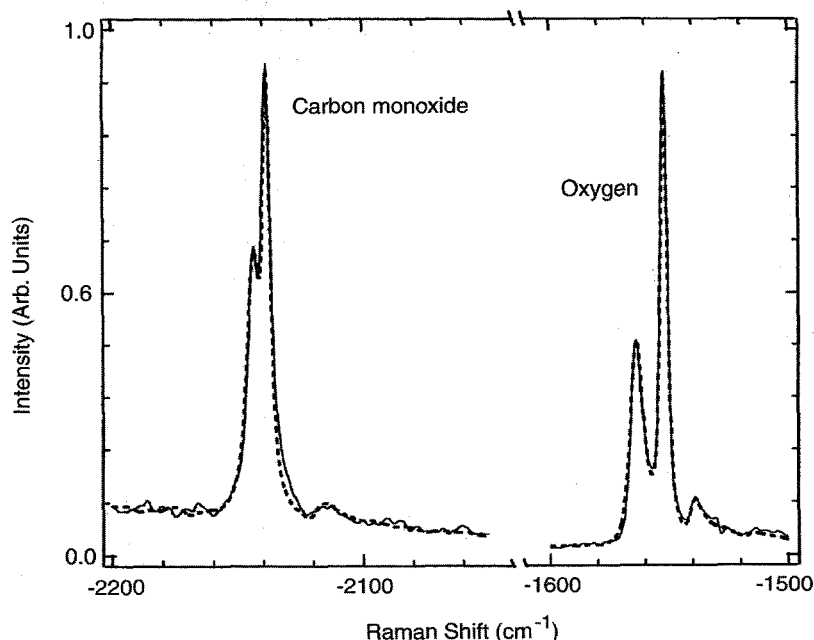
carbon monoxide/oxygen and nitrogen/oxygen mixtures. The experimental spectra were compared with synthetic spectra calculated with a semiclassical model for CARS intensities and using best-fit vibrational frequencies, peak Raman susceptibilities, and Raman linewidths for each mixture component. Up to a maximum shock pressure of 7 GPa for the carbon monoxide/oxygen mixtures and 13 GPa for the nitrogen/oxygen mixtures, the CO, N₂, and O₂ vibrational frequencies were all found to increase monotonically with pressure and depended on the carbon monoxide/oxygen and nitrogen/oxygen mixture ratios. The transition intensity and linewidth data suggest that thermal equilibrium of the vibrational levels is attained in less than 10 ns at these shock pressures.

The vibrational temperatures obtained for the nitrogen/oxygen mixtures were used to improve the oxygen potential function that is used to calculate equation-of-state pressures and temperatures. The measured linewidths for CO, N₂, and O₂ were different for the different mixtures, but did not appear to depend significantly on mixture ratios. The broadening of all spectral lines suggested that the vibrational dephasing time for each species decreased to a few picoseconds at the highest-pressure shock states.

The accompanying figure shows representative CARS spectra of a liquid 67% CO/33% O₂ mixture shock-compressed to 6.8 GPa at a temperature of 1286 K.

Publications

Schmidt, S.C., D.S. Moore, and M.S. Shaw, "Coherent Anti-Stokes Raman Spectroscopy of Shock-Compressed Liquid Carbon Monoxide/Oxygen and Nitrogen/Oxygen Mixtures" (to be published in *J. Chem. Phys.*).



Representative coherent anti-Stokes Raman spectra of a liquid 67% CO/33% O₂ mixture shock-compressed to 6.8 GPa at a temperature of 1286 K. The tall sharp features are the spectra of unshocked carbon monoxide and oxygen, and the lesser peaks are the vibrational progressions from the shocked fluids. The solid curves are the experimental data, and the dotted curves are computed spectra.

Catalysts for Hydrocarbon Oxidation

Kevin Ott

We are investigating the structure and reactivity of site-isolated catalysts that selectively oxidize hydrocarbon substrates. As the starting point for our studies, we are examining a prototypical site-isolated oxidation catalyst, TS-1. TS-1 selectively oxidizes hydrocarbon substrates to useful products using hydrogen peroxide as the oxidant. TS-1 is a microporous silicate with a small percentage of the silicon atoms replaced by titanium.

The titanium ions promote the oxidation chemistry via hydroperoxide intermediates. We are incorporating additional metal ions capable of activating and utilizing molecular oxygen into the structure of TS-1 and similar compounds. It is necessary to know the placement of secondary metal ions such as cobalt, iron, manganese, and chromium with respect to the titanium ions. Because x-ray diffraction techniques are not useful in determining the location of

titanium, we have used neutron diffraction to determine that there is a surprising nonrandom distribution of titanium in the lattice.

We are applying a novel technique called Pair Distribution Function (PDF) to zeolites. PDF is an analysis of diffuse neutron scattering to obtain information about local structure of materials rather than the long-range order afforded by more conventional diffraction experiments. We are primarily interested in the local structure of the titanium ions in TS-1. Preliminary results indicate the PDF data include shifts to larger distances relative to the published data on silicalite, a material analogous to TS-1 but that does not contain titanium. We believe these shifts are likely due to Ti-O bond lengths that are longer than Si-O bond lengths. Knowledge of the structure of the active site is fundamental to understanding the function of any catalyst. We have designed and constructed a

catalytic reactor to be installed this fall into the High Intensity Powder Diffractometer, an instrument for determining the structure of materials, at the Los Alamos Neutron Science Center. This catalytic reactor will allow us to obtain diffraction and PDF data on catalyst structures during reaction.

Publications

Szanyi, J., and M. Paffett, "The Adsorption of NO and Reaction of NO with O₂ on H-, NaH-, CuH-, and Cu-ZSM-5: An In Situ FTIR Investigation," *J. Catal.* **194**, 232-245 (1996).

Szanyi, J., and M. Paffett, "Coadsorption of Nitriles and CO on Cu-ZSM-5: An In Situ FTIR Spectroscopic Study" (to be published in *Mater. Res. Soc., Symp. P Proc.*).

Szanyi, J., and M. Paffett, "A FTIR Investigation of the Coadsorption of Acetonitrile and CO on Cu-ZSM-5" (to be published in *Faraday Transactions of The Chem. Soc.*).

Fundamental Studies of Polymer Filtration

Barbara F. Smith

The objectives of this project are to develop an enhanced fundamental understanding of the coordination chemistry of hazardous-metal-ion complexation with water-soluble metal-binding polymers and to exploit this knowledge to develop improved separations for analytical methods, metals processing, and waste treatment.

We investigated features of water-soluble metal-binding polymers that affect their binding of and selectivity for selected transition metal ions. We evaluated backbone polymers using light-scattering and ultrafiltration techniques to determine the effect of pH and ionic strength on the molecular volume of the polymers. First, we

incrementally functionalized the backbone polymers with a metal-binding ligand. Then we developed a procedure and analytical method to determine the absolute level of functionalization and correlated the results with the elemental analysis, viscosity, and molecular size. We will use these results as a quality assurance measure for these polymers once we transfer them to our industrial partner for commercialization.

Next, we performed a large-scale synthesis of the optimized polymers to confirm that there were no problems with scale-up of the synthesis. Both large- and small-scale synthesis produced the same materials. We did

further troubleshooting with our industrial partner to help get a large-scale pilot unit of the polymer filtration technology installed in a large electroplating facility. The problem addressed involved determining the effect of chromium(VI) on nickel(II) binding to the polymers.

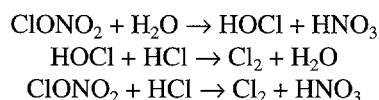
Publications

Smith, B.F., T.W. Robison, et al., "Polymer Filtration: A New Technology for Selective Metals Recovery" (SUR-FIN95 Conference of the American Electroplaters and Surface Finishers Society, Baltimore, Md., June 26-29, 1995).

Modification of Heterogeneous Chemistry by Realistic Substrate Complexity

Bryan Henson

This project explores a set of chemical reactions on porous surfaces that play an important role in the observed depletion of stratospheric ozone over Antarctica every polar spring. We specifically study a series of coupled heterogeneous reactions of chlorine nitrate (ClONO_2) that are of considerable current interest in polar ozone depletion:



These reactions proceed on polar stratospheric clouds which form during the winter, releasing Cl_2 gas that subsequently attacks ozone when sunlight returns during the spring.

We have developed a model of heterogeneous reactivity based on physical adsorption. This model describes how the observed relative humidity affects the reactivity of ClONO_2 with H_2O and HCl on sulfuric acid tetrahydrate (SAT) ice

surfaces and with H_2O on nitric acid trihydrate (NAT) surfaces. For a given system, we model the laboratory data using only two parameters: the measured reaction probability on a neat ice surface and a constant from Brunnauer-Emmett-Teller (BET) theory. This theory describes the fraction of an acid-hydrate surface covered by water as a function of relative humidity. The agreement between calculations of reaction probability based on this model and laboratory measurements is shown in the accompanying figure.

We have used a surface-specific laser technique to quantify the coverage of water on a porous NAT surface. Thus, for the hydrolysis of ClONO_2 on NAT, all parameters in the model are fixed by laboratory measurements. The model indicates that ClONO_2 reactivity with both H_2O and HCl on SAT and with H_2O on NAT is controlled by the surface coverage of H_2O . Our model suggests

that the reported reactivities of HCl with ClONO_2 on NAT may be underestimated by as much as a factor of 10.

Publications

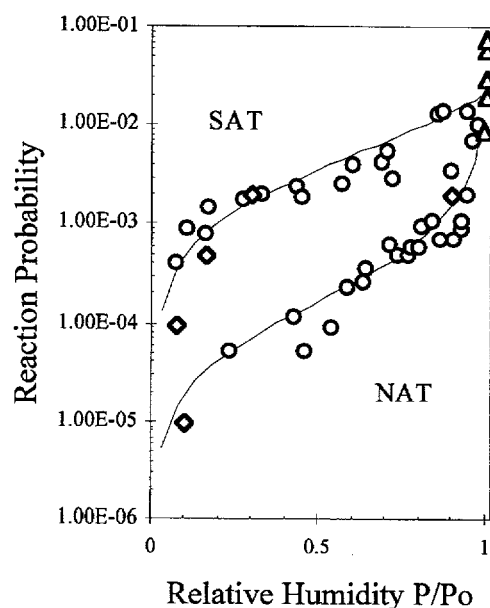
Henson, B.F., K.R. Wilson, and J.M. Robinson, "Chlorine Nitrate Reactivity on Simulated Polar Stratospheric Cloud Surfaces" (211th American Chemical Society Meeting, New Orleans, La., March 1996).

Henson, B.F., K.R. Wilson, and J.M. Robinson, "Modeling the Relative Humidity Dependence of ClONO_2 Reactivity on Ices" (1996 International Symposium on the Physics and Chemistry of Ice, Hanover, N.H., August 1996).

Henson, B.F., K.R. Wilson, and J.M. Robinson, "Modeling the Relative Humidity Dependence of Heterogeneous Reactions on Polar Stratospheric Clouds" (1995 Fall Meeting of the American Geophysical Union, San Francisco, Calif., December 1995).

Henson, B.F., K.R. Wilson, and J.M. Robinson, "A Physical Adsorption Model of the Dependence of ClONO_2 Heterogeneous Reactivity," *Geophys. Res. Lett.* **23**, 1021 (1996).

Henson, B.F., K.R. Wilson, and J.M. Robinson, "Thermodynamics of Heterogeneous Surfaces from Nonlinear Light Scattering" (New Mexico Chapter of the American Vacuum Society Annual Meeting, Albuquerque, N.Mex., April 1996).



The hydrolysis of ClONO_2 on NAT and SAT surfaces. The data are plotted by reaction probability as a function of fractional relative humidity. The curve through the NAT data is calculated from our physical adsorption model with no variable parameters. The curve through the SAT data is a best fit using the same model, which predicts that the coverage of water on SAT is parameterized by the BET constant, $c = 0.2$. The data are from several different laboratories, as referenced in Henson *et al.*, *Geophys. Res. Lett.* **23**, 1021 (1996).

Ionically Conducting Polymers for High-Energy-Density Batteries

Robert Hermes

Using polymer synthesis and electrochemical characterization techniques, we set out to understand the ionic transport chemistry of the polyelectrolyte component of solid-state lithium batteries. Lithium-ion transport is the mechanism by which charge is carried through the polyelectrolyte.

This year we synthesized several oligooxyethylene-modified polyphosphazenes and tested them for electrical conductivity and lithium-ion transport characteristics, each at several lithium-imide-salt loadings and temperatures, under drybox conditions. With fresh batches of

polyelectrolytes, we reproduced the outstanding electrical conductivity results achieved in 1995 and were able to double the room-temperature conductivity from 1.1×10^{-4} S/cm to 2.2×10^{-4} S/cm with two newly synthesized polyelectrolytes.

This result has validated the essence of our original hypothesis: mixed ether side-chains for increased mobility and decreased lithium salt together induce crystallinity. We obtained Raman spectra from various salt/polyelectrolyte compositions.

This spectroscopic technique helped us correlate the ion-pairing threshold of lithium salts with the electrical conductivity results. We also investigated lithium nuclear magnetic resonance as a tool to estimate ionic diffusion coefficients.

In the three years of this project, we have developed techniques that can be used to predict the interaction of lithium and lithium-imide salt with the polyelectrolytes we synthesized in our laboratory. We also achieved the highest room-temperature conductivity for an "unplasticized" solid polyelectrolyte.

Advanced Polymer Chemistry of Organometallic Anions

Rebecca M. Chamberlin

The objective of the project was to prepare and characterize new polymers incorporating the cobalt dicarbollide anion, $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$. Cobalt dicarbollide is well known as an extraction agent for removing radioactive cesium and strontium from nuclear waste. Polymers containing cobalt dicarbollide in the main chain are expected to have novel applications in ion exchange, catalysis, and medical radiotherapy.

During this year we characterized the scope and stereochemical outcome of the twofold deprotonation and nucleophilic substitution reactions of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ and generated a publication on this topic. We also synthesized several reactive monomers using nucleophilic substitution

reactions, most notably a dicarboxylic acid, $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{10})_2(\text{COOH})_2]^-$. The dicarboxylic acid forms organometallic polymers via condensation with amines such as hexamethylene diamine, by two different routes. The first route is conversion of the dicarboxylic acid to a di(acid chloride), which reacts with the diamine in solution to form an insoluble, red polyamide. The second route is direct reaction of the dicarboxylic acid with the diamine, forming an amine salt. The amine salt is thermolyzed in a thermogravimetric analysis/differential thermal analysis (TGA-DTA) experiment to form the polymer while releasing water.

Publications

Balaich, G.J., S.A. Fino, et al., "Synthesis of an Organometallic Polyamide of Cobalt Dicarbollide" (submitted to *Inorg. Chem.*).

Chamberlin, R.M., B.L. Scott, et al., "Butyllithium Deprotonation Versus Alkali Metal Reduction of Cobalt Dicarbollide: A New Route to C-Substituted Derivatives" (to be published in *Inorg. Chem.*).

Reaction Kinetics Relevant to the Recycle Hydride-Dehydride Process for Plutonium Recovery

John Haschke

Objectives of this project were to expand fundamental knowledge of plutonium chemistry and to develop information for enhancing plutonium recovery methods and weapons safety. Plutonium oxide monohydride, PuO(H) , is a novel, but incompletely characterized, compound that forms when plutonium metal is exposed to water. Like other compounds of plutonium(III), it is expected to be highly reactive with oxygen and can promote reactions between metal and air in a manner similar to that observed for plutonium hydride.

Therefore, formation of an oxide hydride layer by reaction with water may catalytically enhance the oxidation of plutonium while avoiding safety problems associated with using hydrogen in the recycle process.

We used pressure-volume-temperature experiments to produce a surface layer of PuO(H) by aqueous corrosion of plutonium metal. We then tested the behavior of moist and dried samples by rapid exposure to oxygen and air. Results of these kinetic studies demonstrate that the monoxide monohydride is pyrophoric when dry

and acts as an initiator for hydride-catalyzed reaction of the metal with air. This process consumes both oxygen and nitrogen and continues until reactants are depleted. The catalyzed corrosion rate of plutonium is 10^8 times faster than the corrosion rate of the metal in dry air. The hydride-catalyzed reaction transforms plutonium into a fine oxide nitride powder with a high potential for aerosolization and environmental dispersal. Catalyzed reaction with oxygen produces plutonium dioxide, the chemical form needed to prepare mixed-oxide fuel for nuclear-power generation, and is potentially applicable as a method for direct recovery of plutonium as PuO_2 . Wet PuO(H) is nonpyrophoric, and the safety hazard posed by formation of oxide hydride is reduced if the material remains moist.

Ultrafast Laser Studies of Solution Reactivity

William Woodruff

Fast chemical dynamics generally must be initiated photochemically. This fact limits the applicability of modern laser methods for following the structural changes that occur during chemical and biological reactions to those systems that have an electronic chromophore that produces a significant yield of photoproduct when excited. Our project has developed a new and entirely general approach to ultrafast initiation of reactions in solution: laser-induced temperature jump. This approach opens entirely new fields of study of ultrafast molecular dynamics in solution.

We have demonstrated the temperature-jump technique on timescales of 50 ps and longer and have applied it to the study of fast events in protein

folding. We have found that a general lifetime of alpha-helix formation is about 100 ns and that tertiary folds (in apomyoglobin) form in about 100 μs . This work has been reported in two publications.

Publications

Gilmanshin, R., S. Williams, R. Callender, et al., "Fast Events in Protein Folding: Relaxation Dynamics of Secondary and Tertiary Structure in Native Apomyoglobin" (to be published in *Proc. Nat. Acad. Sci.*).

Williams, S., T. Causgrove, R. Gilmanshin, et al., "Fast Events in Protein Folding: Helix Melting and Formation in a Small Peptide," *Biochem.* **35** (3), 691-97 (1996).

Mathematics and Computational Sciences

Parallel Three-Dimensional Spherical-Harmonics Transport Methods

Jim Morel

Solution of the Boltzmann transport equation is essential in modeling a wide variety of physical phenomena. The standard angular discretization technique used in production transport codes is the S_n , or discrete-ordinates, method. However, this method does not preserve the rotational invariance of the transport operator, and hence gives rise to nonphysical "ray effects." Such ray effects make the S_n discretization unsuitable in problems with localized sources and optically thin regions. In addition, fundamental

difficulties arise in applying the S_n discretization on finite-element meshes because many cells in typical meshes are re-entrant. The P_n , or spherical-harmonics, method is the only deterministic method that preserves the rotational invariance of the analytic transport operator. The P_n method does not suffer from ray effects and can be applied on finite-element meshes.

The primary goal of our project is to develop three-dimensional, unstructured-mesh radiation transport

algorithms and an associated parallel code based upon a P_n , or spherical-harmonics, discretization in angle. Such a capability is unique to Los Alamos as well as to the entire DOE complex.

This year we completed a parallel P_n code for the Connection Machine 5 computer. This code is based upon a new self-adjoint form of the transport operator that offers significant advantages over previous forms. We also generalized our parallel algorithm, which used unstructured tetrahedral meshes, to use unstructured meshes of arbitrary combinations of hexahedra and degenerate hexahedra, e.g., wedges, pyramids, and tetrahedra.

Adaptive, Composite, Overlapping Mesh Algorithms on Message-Passing Architectures

David L. Brown

We have developed computational methods and a programming framework for adaptive, composite, overlapping meshes to be used on serial and parallel computers. The need for high-level tools to aid in the modeling of large-scale, complex, physical processes described in complex geometries by fluid-flow equations prompted this research. Parallel tools are based on object-oriented, message-passing techniques. We used an object-oriented approach based on the C++ language to create the *Overture* programming framework

in which relatively high-level computational objects may be assembled into solvers for partial differential equations (PDEs). With this framework users can create solvers that are portable across a wide variety of computer architectures and seamlessly incorporate software that uses adaptive, composite overlapping meshes.

We developed a number of C++ class libraries as part of this project. The A++/P++ library handles basic array operations required in scientific

codes. Parallel infrastructures are hidden from the user of this library. The *Overture* framework contains C++ class libraries that handle overlapping meshes, arrays of data on those meshes, and difference operators. We developed PDE codes for compressible and incompressible flow problems as well as an "all-speed" solver that handles flows with a range of Mach numbers from near zero to Mach 1 using these class libraries.

Publications

Brown, D.L., and W.D. Henshaw, "Overture: An Advanced Object-Oriented Software System for Moving Overlapping Grid Computations" (NASA Computational Aerosciences Workshop, Ames, Calif., August 1996).

A Self-Consistent Multiscale Theory of Internal-Wave, Mean-Flow Interactions in the Ocean

Darryl D. Holm

This research is directed toward applications of nonlinear dynamics and kinetic theory in developing new model equations and better analysis tools for nonlinear problems, such as ocean dynamics, involving multiple time- and length-scales. At present it is not feasible to resolve all of these scales and their interactions in numerical simulations. We propose a fundamental approach for describing the effects of these interactions by developing a self-consistent multiscale theory of internal-wave, resolved-flow interactions. To do this, we take advantage of the remarkable statistical homogeneity of the internal wave field observed nearly everywhere in the ocean—the empirical Garrett-Munk spectrum.

We have derived a hierarchy of approximate models of wave, mean-flow interaction (WMFI) for modeling ocean dynamics by using asymptotic expansions. One small parameter for these expansions is the ratio of time scales between internal waves at most wave numbers and the mesoscale mean-flow of an inviscid, stratified, rotating fluid. This “adiabatic ratio” is small and is comparable to the ratio of space scales for the class of initial conditions that support internal waves. Another small parameter available in these expansions is the ratio of the internal-wave amplitude to its wavelength.

The new self-consistent WMFI equations are derived in two ways: first, by requiring Euler’s equations to preserve the wave, mean-flow decomposition to linear order in the wave amplitude; and second, by substituting this decomposition into Hamilton’s principle for Euler’s equations and applying asymptotic expansions and phase averaging to the decomposition. The derivation from

Hamilton’s principle shows that the resulting equations possess a Kelvin circulation theorem, conserve a potential vorticity, and are Lie-Poisson Hamiltonian dynamical systems in the Eulerian variables. The derivation from Euler’s equations confirms the validity of the derivation from Hamilton’s principle. Passage to the Lie-Poisson Hamiltonian formulation brings the WMFI theory into a framework in which formal and nonlinear stability analysis can be applied.

We have also found relations of these results to the Charney-Drazin nonacceleration theorem, Whitham averaging, Wentzel-Kramers-Brillouin (WKB) stability theory, and Lagrangian-mean fluid equations for

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Geometry in the Large and Hyperbolic Chaos

Brosl Hasslacher

Chaos theory continues to be central to the modeling and understanding of complex mathematical and real systems, and the tools being developed to model these systems continue to expand. This project is aimed at providing an important new capability to better understand such systems. In strongly chaotic systems, one common difficulty is that the calculation of useful observables is often blocked by the lack of a workable orbit classification for such systems. This is because global geometrical information from the

original dynamical system is entangled in an unknown way throughout the orbit sequence.

This year we have successfully used geometrical methods from modern mathematics and recent connections between global geometrical and modern quantum field theory to study the natural geometrical objects belonging to hard chaos, i.e., hyperbolic manifolds. In this way we can better interpret global geometrical information and so ultimately calculate useful observables in chaotic systems that otherwise would not be possible.

Industrial Processing of Complex Fluids: Formulation and Modeling

James Scovel

Many commercial materials such as textile fibers, plastics, and fiber-optic cable are produced by cooling complex fluids to form a solid. We are developing models that can be used to optimize the macroscopic properties of such materials and to identify and thus minimize sources of defects.

The objective of our project is to derive constitutive laws of complex fluids in which the relaxation modes are determined geometrically by the different micro-, meso-, and macro-scale structures, and thus the modes couple not only through the dissipative term but through geometrical relations. In addition, the coupling should evolve through the solidification phase.

We developed a model for the two-scale system (where the two scales are fine and coarse) based on a state-space representation in which the transition equation must be modified so that the observation equation corresponds to the mapping from the fine to the coarse scale. The traditional state-space representation consists of two components: the first component is a state vector that cannot be observed but for which the dynamics (the transition equation) is understood. The second component is a mapping from the state vector to a vector of observable quantities. For linear equations of motion, solutions of this system can be found by using the Kalman filter when the equations

of motion on the fine scale are known. When these equations are not precisely known, they can be determined within a particular class by combining the Kalman filter with a maximum-likelihood technique that we have developed. However, how to apply this technique in the case of nonlinear equations of motion has not been determined.

To test our maximum-likelihood technique, we applied it to the unsolved problem of disaggregation of time series. We developed and tested an algorithm for the disaggregation of time series on several classes of data generated by Auto Regressive Integrated Moving Average (ARIMA) processes. We found that we can successfully estimate the parameters of the model generating the original data from the aggregate data alone. In addition, our estimates of the disaggregate data are superior to a naive estimate commonly used in multigrid methods.

Dispersive Water Waves in One and Two Dimensions

Darryl D. Holm

With applications in mind for geophysical ocean dynamics, we are using multiple-time-scale perturbation theory to derive new equations for the long-time asymptotic behavior of dispersive shallow-water flow in a thin domain over a varying bottom in one and two dimensions. This past year we continued to analyze our new shallow-water equations and related systems of equations while developing new directions for the mathematics underlying the integrability of these systems. In particular, we applied the generating equation method to create and study new integrable systems of nonlinear partial differential equations related to our shallow-water equations. We also investigated the solutions of these systems of equations on a periodic spatial domain by using methods from

the complex algebraic geometry of Riemann surfaces.

We developed several aspects of the required mathematical tools in the course of this investigation: (1) inverse scattering with degenerate potentials, (2) asymptotic reduction of the angle representations, (3) geometric singular perturbation theory, and (4) modulation theory and singularity tracking for completely integrable equations.

We also studied models that admit weak solutions, i.e., solutions with discontinuous derivatives in the form of corners or cusps. These appear even though the models we are studying are integrable, a property that is often incorrectly assumed to imply smooth solution behavior. We also derived new shallow-water equations in two dimensions. These equations provide an estimate of the

long-time asymptotic effects of slowly varying bottom topography and weak hydrostatic imbalance on the vertically averaged, horizontal velocity of an incompressible fluid with a free surface moving under the force of gravity. In this work we considered the regime in which the Froude number is much smaller than the aspect ratio of the shallow domain.

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Mimetic Difference Approximations of Partial Differential Equations

James Hyman

The goal of this research has been to construct local, high-order difference approximations of differential operators on nonuniform grids that mimic the symmetry properties of the continuum differential operators. Partial differential equations solved with these mimetic difference approximations automatically satisfy discrete versions of conservation laws and of analogies to Stoke's theorem; because these versions are true in the continuum, they are more likely to produce physically faithful results. Continuum symmetries are easily preserved by local, discrete high-order approximations on uniform grids, but they are difficult to retain in high-order approximations on nonuniform grids. The approximations must also be local and use only function values at nearby points in the computational grid; these methods are especially efficient on computers with distributed memory.

We have derived new, mimetic, fourth-order, finite-difference discretizations of the divergence, gradient, and Laplacian on nonuniform grids. The discrete divergence is

the negative of the adjoint of the discrete gradient, and consequently the Laplacian is a symmetric negative operator. The new methods we are deriving are local, accurate, reliable, and efficient difference methods that mimic symmetry, conservation, stability, the duality relationships, and the identities between the gradient, curl, and divergence operators on nonuniform grids. These methods are especially powerful on coarse nonuniform grids and in calculations in which the mesh moves to track interfaces or shocks, such as in modeling fluid dynamics.

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Wavelet Transforms as Solutions of Partial Differential Equations

George Zweig

A significant recent development in applied mathematics is the study of wavelet transforms, both continuous and discrete. Like Fourier transforms, wavelet transforms express functions in terms of simple building blocks; in particular, wavelet transforms decompose functions into components with respect to a set of expansion functions that are dilations and translations of a single function called

the "parent wavelet." Such wavelet transforms are useful in representing "transients" whose time and frequency structure reflects the dynamics of an underlying physical system. Speech sound, pressure in turbulent fluid flow, or engine sound in automobiles are excellent candidates for wavelet analysis.

We made significant progress in two areas: (1) methods for choosing

the parent wavelet for a continuous wavelet transform in pattern recognition applications were developed, and (2) the computation of continuous wavelet transforms was made more efficient by understanding the relationship between discrete wavelet transforms and discretized continuous wavelet transforms.

Publications

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Dispersive, Internal, Long-Wave Models

Roberto Camassa

This work is a joint analytical and numerical study of internal, dispersive water-wave propagation in a stratified two-layer fluid, a problem that has important geophysical applications. Two-layer models can capture the main baroclinic (density dependent) effects. They also support the observed large-amplitude, internal wave motion at the interface between layers as well as a large shear in the velocity field, which cannot be described by the simpler barotropic (vertically integrated) models.

We have derived model equations for two-layer, stratified fluid in the fully nonlinear regimes for finite and infinite depth of the lower layer. By considering the weakly nonlinear regimes in various limits of the ratio

between upper and lower layer depths, and by assuming unidirectionality of wave propagation, we have shown that our model equations reduce to the known cases of coupled Boussinesq, intermediate long-wave, and Benjamin-Ono equations. We have implemented finite-difference and pseudo-spectral codes for solving numerically the traveling wave solutions for the one-dimensional version of the model and also carried out simulations of interacting waves.

One breakthrough made possible by retaining the full nonlinearity of the fundamental dynamics of the two-layer fluid finally clarifies experimental observations that have been left unexplained for more than 15 years. It

is now evident that the traditional weakly nonlinear models are unable to deal with most regimes encountered experimentally. However, these regimes can be accurately described by our new equations, with minimal loss of simplicity with respect to the known models.

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Solution-Adaptive Methods for Low-Speed and All-Speed Flows

Jeffrey S. Saltzman

We are developing solution-adaptive methods for efficiently computing fluid problems that involve low-speed flows and problems that are a mixture of low-speed and high-speed flows. A solution-adaptive method switches to different solvers and/or algorithms as needed in different regions of the problem domain. In regions where the flow is slightly compressible (low-speed), we use a scheme based on efficient and accurate methods that have been recently developed for incompressible

flows. In regions of the domain where the flow is compressible, we switch to an existing high-quality shock-capturing method. As another possibility, there may be parts of the domain where only sound waves are present, and in this case we would use a method that is optimized for the wave equation of acoustics.

We have developed and are now comparing two promising approaches for all-speed flow solvers. The first is based on a novel Godunov-Projection algorithm for incompressible flows

that we have extended to treat flows at all Mach numbers. The second approach uses a semi-implicit discretization for low Mach numbers that requires the solution of only one scalar Poisson equation. The latter method switches to a standard compressible solver when the Mach number becomes sufficiently large. We used the "Overture" class libraries to write the solvers; the Overture libraries provide a high-level interface for solving partial differential equations on moving, overlapping grids. This method provides for significant reuse of code between the solvers, meaning that future solvers will be easier to write. The requirements of the solvers have also influenced the design and capabilities of the Overture library.

Combinatorics, Geometry, and Mathematical Physics

William Chen

Combinatorics and geometry are among the most active areas of mathematics today, and this project is particularly focused on the areas of unitary symmetry and combinatorics, q -extensions of hypergeometric functions, and Hopf algebras. These areas of mathematics will continue to be important for the next several decades because of the power they bring both in new techniques and in the linkages that have emerged between them and several established fields. In this work, we extend these linkages to an area of mathematical physics dealing with symmetry and the quantum description of many-particle systems. As a result, we have identified a specific area of applied mathematics with applications to physics, chemistry, and perhaps biology.

During the two years of this project, we have advanced our goal of bringing combinatorics to bear on physical problems by the publication of six papers (three in 1995) dealing with these subjects and by five more papers accepted by refereed journals. These papers are in each of the stated areas of unitary symmetry and combinatorics, q -extensions of hypergeometric functions, and Hopf algebras. We expect that these latter two "hot topics" will feed back to the first one and advance that subject. Finally, we have in advanced stages of preparation nine more papers coming under the purview of our proposal, about half of which have resulted in requests to present our work in invited talks at scientific conferences. We have made and are still making substantive contributions in the cross-fertilization of combinatorics and its applications.

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The Fundamental Role of Solitons in Nonlinear Partial Differential Equations

James Hyman

Numerical simulations and mathematical analysis have proved crucial to understanding the fundamental role of solitons in the evolution of general initial data for quasilinear, dispersive partial differential equations, such as the Korteweg-de Vries (KdV) nonlinear Schrödinger and the Kadomtsev-Petviashvili equations. These equations have linear dispersion, and the solitons have infinite support.

Recently, we discovered a new class of solitons with compact support for similar equations with nonlinear dispersion. These 'compactons' display the same modal decompositions and structural stability observed in earlier integrable partial differential equations. They form from arbitrary initial data, are nonlinearly self-stabilizing, and maintain their coherence after multiple collisions, even though the equations are not integrable.

This year we discovered a new multiple-humped, pulsating soliton for a related fifth-order KdV equation. This multihumped solitary wave shares many of the properties of the traditional single-humped solitons previously seen in KdV-like equations. We have observed multi-humped solitary waves, with up to eleven humps, that are dynamically stable in multisoliton collisions emerge spontaneously from initial data.

We also began a new research project to investigate a new nonlinear dispersive equation based on a Lagrangian approach to another fifth-order KdV-like equation. The solutions of this new family of equations possess a rich variety of compact and noncompact solitons. This research is the opening for a far-reaching and new understanding of the central role of solitons in nonlinear dispersion.

Elliptic Solvers for Adaptive Mesh Refinement Grids

Daniel Quinlan

We are developing multigrid methods that will efficiently solve elliptic problems with anisotropic and discontinuous coefficients on adaptive grids. The final result will be a library that provides for the simplified solution of such problems. This library will directly benefit efforts in scientific computing, geoanalysis, fluid dynamics, mathematical modeling and analysis, radiation transport, and others. The focus of this work is research on serial and parallel elliptic algorithms and the inclusion of our black-box multigrid

techniques into this new setting. The approach applies the Los Alamos object-oriented class libraries that greatly simplify the development.

We focused on the extended development of the software tools for parallel adaptive mesh refinement and their application to a simplified adaptive mesh refinement. The initial application involved the Fast Adaptive Composite and Asynchronous Fast Adaptive Composite solution methods using Multigrid single-grid solvers. We demonstrated that Multigrid solvers (an important component of

the adaptive solvers) can run in parallel using the P++ array class (parallel array class); we originally developed the solvers in the serial environment using the A++ array class (serial array class). This demonstration illustrated the usefulness of the simplified application development environment provided by the object-oriented A++/P++ class libraries. We completed extending P++ for use with adaptive mesh refinement and tested its robustness on different parallel environments.

As part of the AMR++ work (AMR++ is an object-oriented library for adaptive mesh refinement methods), we installed a sophisticated graphics and visualization system that permits simplified debugging and interpretation of adaptive results. This work has proved to be an important tool in the research on numerical algorithms for problems difficult to analyze.

We have nearly completed additional work on parallel load balancing specific to adaptive mesh refinement. This work has focused on fast optimal complexity algorithms for the load balancing and distribution of the adaptive refinement grid across a large number of processors. The algorithms are specific to structured grid adaptive mesh refinement, and we expect them to be applicable to many other parallel structured applications as well.

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Studies of Structure of Turbulence by High-Resolution Simulation and Theory

Shiyi Chen

This project is a study of the structures of fluid turbulence through high-resolution, direct numerical simulation and the development of theory based on those simulations. Significant advances have been made in the study of fundamental fluid turbulence through our numerical and theoretical work.

Using the equations of motion, we have predicted analytically the scaling exponents for anomalous diffusion involving fluid turbulence, and we have verified these exponents through a large-scale simulation with 8,192 mesh points. This research is the first instance in which anomalous scaling exponents for a turbulence problem have been deduced from the equations of motion.

We carried out high-resolution, direct numerical simulations of three-dimensional (3-D) Navier-Stokes

turbulence with normal and hyperviscosity to study inertial-range statistics. We found that both the scalings and the probability distribution functions are independent of the dissipation mechanism, while the near-dissipation-range fluctuations (smaller-scale motions) show significant structural differences.

We studied the statistics and structures of pressure field, vorticity, and dissipation in 3-D, incompressible, isotropic turbulence. We also investigated the statistical relations among pressure, vorticity, dissipation, and kinetic energy using a conditional averaging process. Finally, we studied the conditionally averaged velocity increments as a function of the locally averaged dissipation. Our results provide direct evidence that supports the refined similarity hypothesis.

Computational Three-Dimensional Inversion for Seismic Exploration

Eugene Gavrilov

We are working to develop and implement a three-dimensional computational inversion tool for seismic exploration that will significantly improve the effectiveness of current seismic technology. Our technique allows more efficient data gathering and analysis and, most important, automates the current inversion process, eliminating the current need for human "interpreters." In addition, our technique has the potential to dramatically improve medical imaging technology for shortwave diagnostics.

We modified a three-dimensional acoustic code for the massively parallel

computer, Cray T3D, that was implemented at the Advanced Computing Laboratory; the code will serve as a test tool that we can use to solve the forward problem, whose solution is critical to solving the inverse problem. We used the three-dimensional forward code to explore three different methods for solving the inverse problem, or the inversion process.

Unfortunately, the first method, based on the inverse matrix, was unstable for three-dimensional cases and did not produce the expected results. The second method, three-dimensional computational acoustic holography, allowed us to convert

seismic (acoustic) records into a visual representation of the explored medium. This method was stable and robust, and although it did not provide an accurate velocity distribution because of a phase shift, it nevertheless captured the major features of the velocity structure. In fact, this method could be of great use in ultrasound medical imaging. The third method we explored was based on the coupled-phase (eikonal) and amplitude equations. With this method we were able to recover the phase from records and then solve the amplitude equation for the whole investigated domain, thereby achieving an accurate mathematical representation of the undistorted velocity in three dimensions. Our initial results from this method are very promising, but we must explore it further to verify its usefulness and effectiveness.

Super-Speed Computer Interfaces and Networks

Donald Tolmie

Researchers studying super-speed computer interfaces and networks have focused on identifying the networking requirements of computation-intensive applications that are critical to DOE programs. In particular, both the Energy Research, High-Performance Computing Research Centers (HPCRCs) and the Defense Programs, Accelerated Strategic Computing Initiative (ASCI) have planned applications that will require large increases in network bandwidth. In

this project we were working to identify and understand critical requirements and to explore ways to develop super-speed networks. When the necessary network components become available, we plan to conduct early experiments on network switch and diagnostic techniques.

According to application developers at Los Alamos and other research institutes, the new super-speed network requirements fall in the 5- to 10-Gbit range. We have also identified

another parameter, network latency, as being critical to these applications. For the applications to perform well, we estimate that a network latency of less than 1 μ s is the upper bound.

For this project we have performed an exhaustive evaluation of current network technologies. Based on the criteria above, we found that no single technology meets all of the requirements. This finding triggered a collaboration of Los Alamos researchers with computer and networking vendors to develop a 6.4-Gbit network specification called HIPPI-6400. We are leading the effort to develop the HIPPI-6400 specification as an American National Standard. We have also started to develop a tester to verify and measure the performance of HIPPI-6400 implementations.

Particles and Patterns in Cellular Automata

Erica Jen

We developed a general methodology to study particles and domains in one-dimensional cellular automata. A cellular automaton is a discrete dynamical system that consists of a lattice of sites whose values evolve through a local interaction rule. Newly obtained results in the mathematics of one-dimensional cellular automata promise to provide for the first time a method for analyzing the relationship between an automaton's microscopic-level specification

through its rule table, and certain macroscopic features—including pattern formation and computational capabilities—that characterize its evolution. The central point is that these automata are characterized by their generation of mesoscopic structures that can be viewed as particles and backgrounds, and the global behavior of the automata may be described through a reformulation of the automaton in terms of collision rules on this mesoscopic scale.

On the basis of this methodology, an atlas was generated of the range of backgrounds, particle types, and particle for one particular elementary local interaction scheme. Based on this atlas, an appropriate filter was constructed to study the pattern evolution, self-organization, and computational characteristics of this system. Finally a deterministic description of the filtered system was derived that permits the characterization of interactions resulting in (1) annihilation of particles by backgrounds, (2) annihilation of backgrounds by particles, and (3) spatial translation of particles induced by collisions with backgrounds.

High-Quality Finite-Difference Schemes for Partial Differential Equations and Discrete Vector and Tensor Analysis

Mikhail Shashkov

Our primary goal in this project is to develop new, general techniques for performing large-scale numerical simulations based on approximating the solution of partial differential equations. The basis of these new techniques is the design of discrete operators that preserve certain essential properties of, and relationships between, their corresponding analytic operators. The techniques will significantly extend the well-known and useful finite-volume methods and are designed to more faithfully represent important properties of physical processes and the continuum mathematical models for such processes. Algorithms based on these techniques can be used for modeling high-speed flows, porous-media flows, diffusion processes, and geophysical flows.

This year we constructed discrete analogs of the invariant first-order operators—**div**, **grad**, and **curl**—on a logically rectangular grid and proved discrete analogs of the main theorems of vector analysis related to these

operators. Using discrete analogs of divergence and gradient, we developed new finite-difference schemes for two-dimensional diffusion equations with a discontinuous, nondiagonal matrix of coefficients on a logically rectangular grid. We also tested our new schemes on practical problems. We analyzed problems involving the conservation laws and the presence of parasitic modes in Lagrangian codes, formulating these problems in terms of vector and tensor analysis. Our goal is to find the relationship between the desired properties of finite-difference schemes (i.e., maintaining conservation laws but suppressing parasitic modes) and the properties of the objects of vector analysis.

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Modeling Mesoscopic Phenomena in Extended Dynamical Systems

Alan Bishop

Our research goals were to develop appropriate analytical and numerical techniques to describe the formation and dynamics of collective, coherent structures in extended nonlinear dynamical systems and their role in macroscopic space-time complexity. The influence of nonlinearity, classical and quantum stochasticity, and lattice discreteness has also been addressed and classified in some cases.

Our major achievements were as follows:

- We have obtained classes of nonlinear solutions on curved geometries that demonstrate a novel interplay between topology and geometric frustration relevant for nanoscale systems.
- We have analyzed the nature and stability of localized, oscillatory nonlinear excitations (multiphonon bound states) on discrete nonlinear chains, including demonstrations of successful perturbation theories, existence of quasiperiodic excitations, response to external statistical time-dependent fields and point impurities, robustness in the presence of quantum fluctuations, and effects of boundary conditions.
- We have demonstrated multi-timescale effects for nonlinear Schrödinger descriptions and have shown the success of memory function approaches for going beyond these approximations.
- In addition we have developed a generalized rate-equation framework that allows analysis of the important creation/annihilation processes in driven nonlinear, nonequilibrium systems.

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Atomic and Molecular Physics

State-to-State Photodetachment in the Two-Electron Hydrogen Ion

Charlie E. M. Strauss

Experimental observation of the negative hydrogen ion, which consists of only two electrons and a proton, is fundamentally important to the development of three-body quantum mechanics. We have observed the negative hydrogen ion in a regime in which the optical electric fields are becoming comparable to the binding fields of the ion (that is, high-field physics). The principal objective of observing the low-field one-photon spectroscopy of the negative hydrogen system was overshadowed by our observation of two new physical processes.

First, the negative hydrogen system exhibited multiphoton excitation to a

detachment resonance. This is the first time that a multiphoton detachment resonance has been seen in a negative atomic ion. The analogous process in neutral atoms, multiphoton ionization, differs from multiphoton detachment resonance because ions exhibit a long-range coulombic binding potential. The yield (as a function of laser wavelength) of electrons ejected with kinetic energy in excess of the single-photon energy showed a pronounced Fano-profile-shaped peak, consistent with theoretical predictions. Second, we observed nonresonant excess photon detachment with photons of energy exceeding the ion's binding energy. Nonresonant excess photon

detachment in competition with the single-photon process was previously unknown in either ions or neutrals.

This year, we also assembled a vacuum ultraviolet (VUV) laser with which to examine, as a function of VUV wavelength and electron energy distribution, the Feshbach and Shape resonances in the negative hydrogen ion near 113 nm. Our collaborators from the University of New Mexico are continuing research on both multiphoton and VUV spectroscopy, and they are searching for similar phenomena in the deuterium analogue.

Publications

Zhao, X.M., M.S. Gulley, H.C. Bryant, et al., "Nonresonant Excess Photon Detachment of Negative Hydrogen Ions" (to be published in *Phys. Rev. Lett.*).

Transient Quantum Mechanical Processes

Lee Collins

The principal objective of this project is the theoretical investigation of transient quantum mechanical events such as coherent control of molecular processes and artificial atoms. Rapid advances in laser technology have made control of quantal processes possible. Since the duration of laser pulses has become much shorter than that of many molecular interactions, a laser will act as a strobe that probes the evolution of the system. Electrons passing through layers of composite materials that are many nanometers thick also behave as quantum mechanical entities, despite the large-scale nature of the medium. However, the study of such transient processes

requires the development of sophisticated, large-scale computational approaches to solve the time-dependent Schrödinger equation, which represents the basic physics of these fleeting encounters. One major goal of our project involves modeling various molecular-control experiments conducted at Los Alamos.

This year, we have developed and extensively tested two independent methods for efficiently and accurately solving the time-dependent Schrödinger equation for these processes. The methods are based on the real-space-product and discrete-variable-representation formulations, respectively. We first applied the methods to

the interaction of a short-pulse laser with a dimer of potassium in order to study the interference effects between vibrational wave packets in different electronic states. Initial calculations using simple models for the molecular interactions yielded qualitative agreement with experiment. They indicated a clear correlation between the signal and the vibrational motion of the wave packet. To improve the agreement, we have begun calculating better molecular parameters such as potential energy curves and coupling matrix elements.

Publications

Collins, L., R. Walker, and J. Kress, "Quantum Control of Molecular Processes," *Bull. Am. Phys. Soc.* **41**, 1145 (1996).

Calculation of Satellite Line Structures in Highly Stripped Plasmas

Joseph Abdallah Jr.

Recently developed high-resolution x-ray spectrographs have made it possible to measure satellite line structures from various plasma sources with great detail. These are weak, optically thin lines caused by the decay of autoionizing states and generally accompany the resonance lines of hydrogen-like and helium-like ions. The goal is to use Los Alamos atomic physics and nonequilibrium kinetics codes to calculate the line structure and compare it with high-resolution experiments. Consequently, we are able to interpret and understand the physical processes in plasma. The results can be used to develop plasma temperature and density diagnostics using the signature of satellite structures. Such diagnostics will have wide application to Laboratory programs. The study also provides a fundamental understanding of the atomic physics processes in different plasma environments. Collaborations with A. Ya Faenov, T. A. Pikuz, and S. A. Pikuz of Russia add tremendous value to the research.

The accomplishments for this year include the analysis of satellite spectra taken from various plasma sources, including a silicon spectrum measured at the Los Alamos Bright Source Facility. We studied data from aluminum X-Pinch experiments performed at Cornell University that showed a strong dependence on electron-beam effects. Data on magnesium have been taken from the Russian Multicharged Ion Spectra Data Center carbon dioxide laser facility and the Los Alamos Trident laser. The observed satellite structures show strong dependence on hot electrons for both the Russian and the Trident laser (500 fs, 1054 nm) measurements. We have determined electron densities, thermal temperatures, and hot-electron fractions by

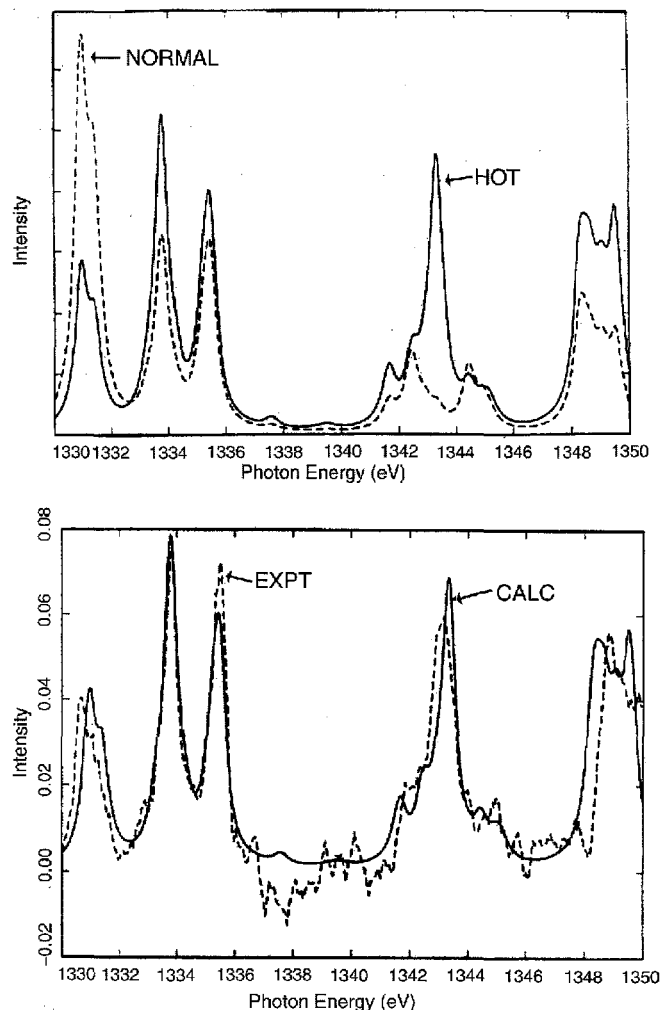
matching the experimental results with calculations.

Model calculations were performed using an electron distribution consisting of a thermal Maxwellian part and a nonthermal, high-energy Gaussian part to determine if hot electrons could be responsible for the anomalous structure of satellite lines observed in the Trident experiments. The first figure is a comparison of the calculated spectra for magnesium shown with and without hot electrons

at an electron temperature near 200 eV and a electron density of $10^{22}/\text{cm}^3$. The number of hot electrons is fixed at 10% of the electron density. Note the significant difference between the relative intensities predicted for the two different cases. The second figure shows the good agreement of the measured Trident spectrum with calculations that include the effect of hot electrons.

Publications

Abdallah, J. Jr., A. Ya Faenov, D. Hammer, et al., "Electron Beam Effects on the Spectroscopy of Satellite Lines in Aluminum X-Pinch Experiments," *Phys. Scr.* **53**, 705 (1996).



(Top) A comparison of calculated spectra for magnesium showing the effect of hot electrons at an electron temperature near 200 eV and a density of 10^{22} electrons per cubic centimeter. (Bottom) A comparison of the calculated spectrum including the effect of hot electrons with the observed Trident spectrum.

Optical Wave Packets (Optical Bullets): A New, Diffraction-Free Form of Light Travel

David J. Funk

In this work we study the propagation of self-confined packets of light through the atmosphere. At sufficiently high intensities, pulses of light will not only self-focus, but may propagate indefinitely without active optics or guiding media in the form of a fine filament until the intensity of the pulse falls below a measurable critical value.

We are analyzing the phase and structure of the pulse above, near, and below that critical intensity to understand the origin of this phenomenon. We are also investigating the use of the filament path as a waveguide for low-intensity laser pulses. The ability to focus intense light at large distances and collect the scattered light may revolutionize active remote sensing and long-range energy transmission. Applications include remote sensing and range finding in battlefield conditions, long-range energy transmission, and guiding lightning discharge.

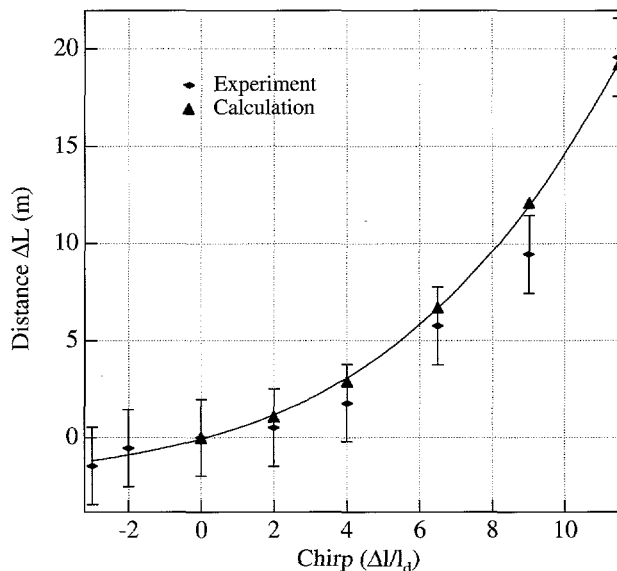
Our studies have concentrated on the demonstration and understanding of the fundamental physics associated with this phenomenon and the proof of the existence of these wave packets in air. We have successfully (1) generated filaments, (2) set up a frequency-resolved, optical-gating analysis station, (3) measured the energy in the filament as a function of travel distance in the laboratory, (4) examined the effect of chirp on the pulse (both on filament formation distance and conical emission), as shown in the first figure, and (5) spectrally dispersed and autocorrelated the filament as a function of distance traveled in the laboratory.

We have also found that the pulse splits into two pulses as it propagates, as predicted by various theories that fold in the nonlinear interaction of intense electromagnetic fields with matter (see second figure). Our goal is to be able to control this phenom-

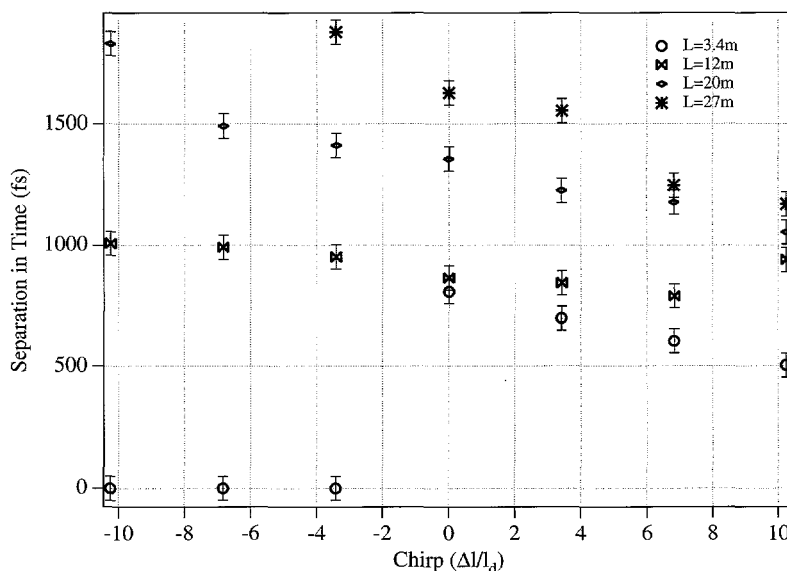
enon and turn it into a useful tool for controlling lightning discharge (as an example) by providing an ionization path for the lightning to discharge along.

Publications

Zhao, X.M., R.J. Jones, D.J. Funk, et al., "Evolution Characteristics and Control of Self-Filamentation in the Atmosphere" (submitted to *Opt. Lett.*).



Effect of chirp on filament formation distance. The graph shows that the pulse forms most readily when blue light precedes red light (large $\Delta\lambda/\lambda_d$) as expected from a simple, group-velocity dispersion analysis.



Effect of chirp on pulse splitting as a function of propagation distance L . The graph shows that the pulse splits most readily when blue light precedes red light (large $\Delta\lambda/\lambda_d$), as expected from a simple, self-phase modulation and group-velocity dispersion analysis.

Nonlinear Atom Optics

Peter Milonni

The objective of this project is to develop the quantum field theory of atom optics and, in particular, to explore the possibilities for realizing nonlinear wave effects in atom optics. Our progress in the basic physics and in the development of very promising applications has been rapid. We are focusing on nonlinear atom-optical effects including wave phenomena such as self-focusing, solitary-wave formation, wave mixing, and phase conjugation, which can arise from long-range dipole-dipole interactions. Such effects occur when more than one atom can occupy a single "mode" of the many-body wave function, a

situation of particular interest in "lasers for atoms" with which relatively intense atom waves, rather than photon waves, will be produced.

We have outlined the basic structure of a coherence theory of atom optics, along the lines of the optical theory of coherence. A few issues involving the treatment of atom-atom interactions remain to be worked out before the theory is written up and submitted for publication. One of the issues is the modification of atom-atom interactions in the case of cold atomic samples that are of interest in atom optics. For the case of ground-state atoms, we have

analyzed the modification of van der Waals interactions in both thermal and laser fields.

The natural framework for the many-particle system of interest, including the two-body dipole-dipole interactions and the quantum statistics, is quantum field theory. In this case, the requisite formalism is nonrelativistic, and it leads to computationally workable, coupled, nonlinear wave equations. We have developed this formalism and are preparing it for publication, following the numerical simulation of a few examples based on the formalism. We have also begun to study the applications of this theory to the recently observed Bose-Einstein condensation in cold atom traps.

Dynamics of Quantum Wave Packets

Timothy R. Gosnell

The time-domain investigation of localized vibrational wave functions in diatomic molecules is possible with femtosecond laser sources. In our experiment, a femtosecond pump pulse creates a wave packet on an excited potential surface of gas-phase K_2 molecules. The packet oscillates within the well, much as one expects classically, but then disperses as a result of rotational effects and dispersion within the the weakly anharmonic potential well. The purpose of the experiment is not just to create and observe such packets but to alter their shape by manipulating

the time and spectral content (or chirp) of the pump pulse. The ultimate goal is to develop a broader tool set for controlling chemical reactions with laser light.

This year we improved the signal-to-noise ratio in our wave-packet detector and confirmed chirp-induced effects on the shape of the packets. A theoretical investigation helped clarify wave-packet dynamics, but continued theoretical studies are needed to understand the specific wave-packet shapes and decay patterns observed in our experiments.

Geoscience, Space Science, and Astrophysics

Low-Energy Neutral Atom Imager

Herbert O. Funsten and
David J. McComas

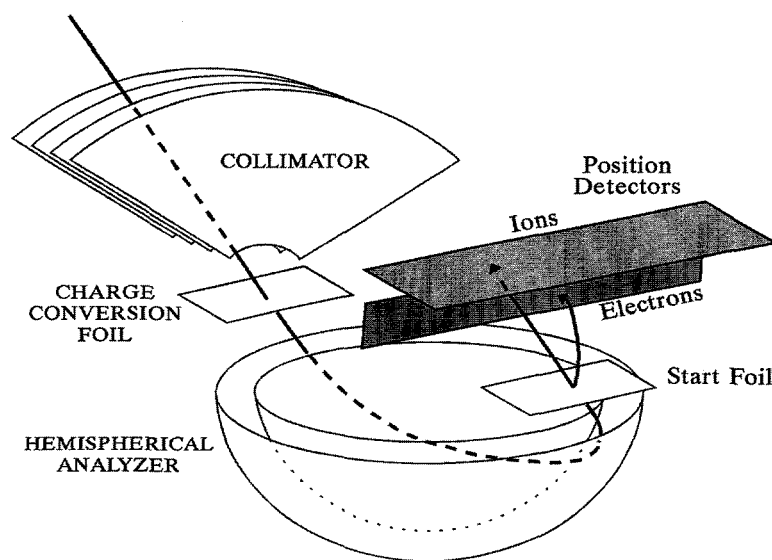
Remote imaging from space is contributing more and more to our understanding of the space environment around Earth. Sensing of magnetospheric plasma ions that have been neutralized by charge exchange with geocoronal neutral atoms promises to be the next major diagnostic of magnetospheric physics and may provide global snapshots of the structure and dynamics of the terrestrial magnetosphere.

The goal of this project is to fly the first low-energy neutral atom (LENA) imager capable of imaging neutral atoms with energies less than 30 keV. As shown in the accompanying figure, the imager consists of (1) alternately biased collimator plates to reject ambient plasma particles, (2) an ultrathin, 50-Å foil that ionizes a fraction of the neutral atoms that transit the foil, (3) electrostatic energy analyzer plates that measure the

LENA energy, and (4) a detector subsystem that provides trajectory and coincidence measurements.

In this first year we have successfully completed the design, procurement, and fabrication of imager components. We assembled and tested the collimator, door, and detector subassemblies. As a demonstration of new technology, the LENA imager uses thin-walled, hemispherical, electrostatic energy analyzer plates that were formed by electroplating, which is considerably less expensive than traditional machining.

The LENA imager, which will be fully flight qualified, is positioned to fly on the first ride of opportunity. The LENA imager will provide the first neutral atom measurements for its energy range with image integration times of several minutes.



Los Alamos low-energy neutral atom (LENA) imager.

Publications

Funsten, H.O., D.J. McComas, and M.A. Gruntman, "Mechanisms for Neutral Atom Imaging" (submitted to Am. Geophys. Union Monograph Series, *Measurement Techniques for Space Plasmas*).

Hesse, M., D. Mitchell, E. Roelof, et al., "Neutral Atom Imaging of the Plasma Sheet: Measurement Predictions" (submitted to *Geophys. Res. Lett.*).

McComas, D.J., H.O. Funsten, and E.E. Scime, "Advances in Low Energy Neutral Atom Imaging" (submitted to Am. Geophys. Union Monograph Series, *Measurement Techniques for Space Plasmas*).

Nonlinear Processes in Earthquakes

Eric Jones

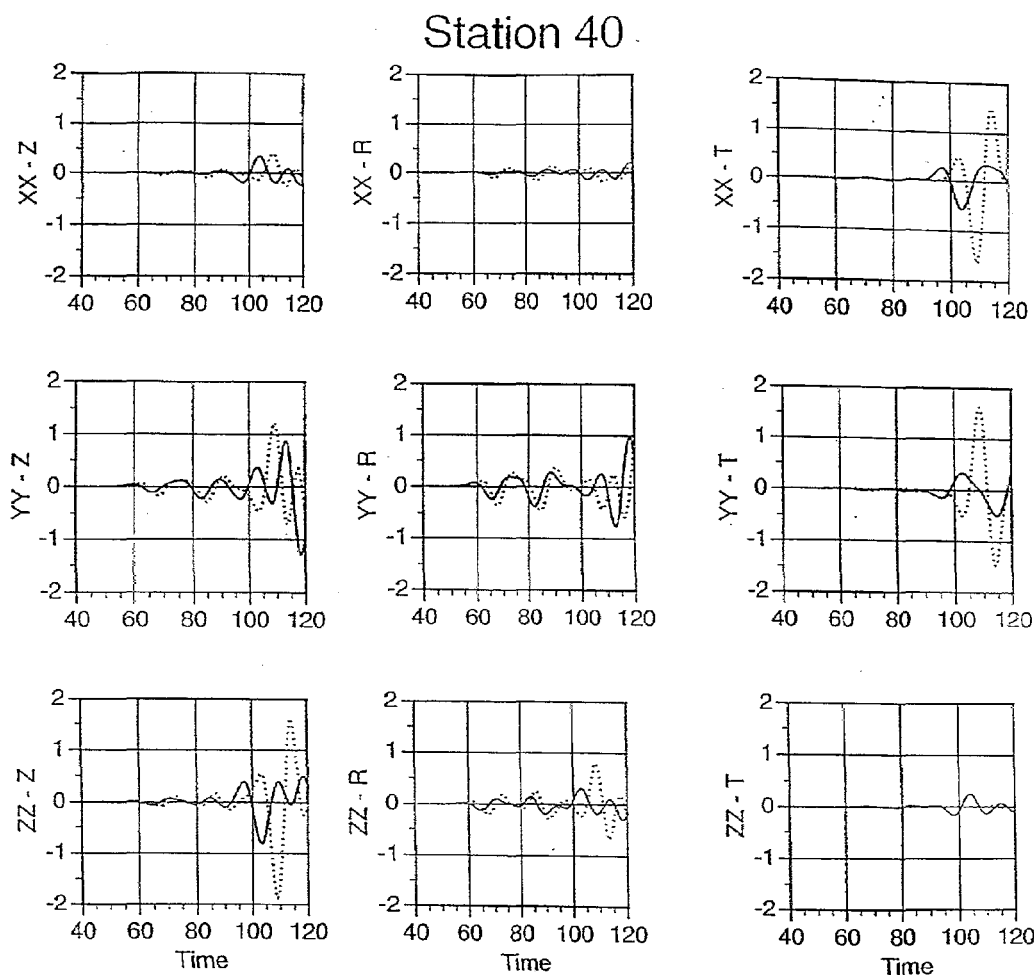
Characterizing the source of seismic signals is important both for distinguishing clandestine nuclear tests from earthquakes and for understanding the mechanisms of earthquakes. However, geologic structures near the source and along the propagation path can modify the seismic signals and complicate source analyses.

We applied a three-dimensional, elastic-wave-propagation code, known as the AFD code, to model an earthquake near the upper boundary of a subducting slab. As shown in the

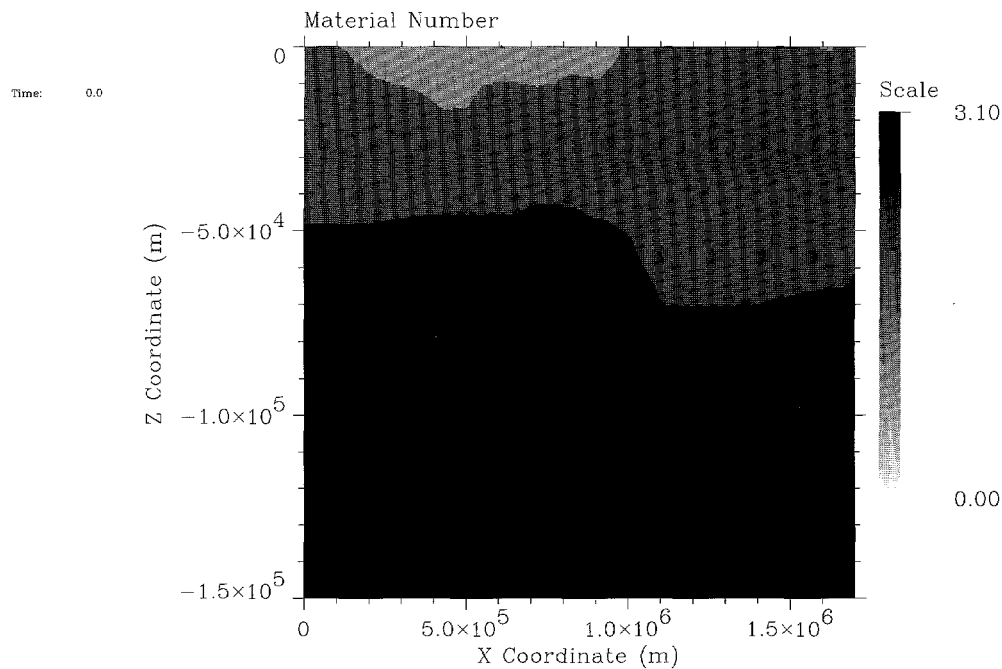
three-dimensional seismograms, the differences between the synthetic seismograms calculated with and without the slab are significant. Our collaborators at the University of Texas planned to use existing analysis techniques to show that inferred seismic moment tensors would contain non-double-couple components. However, by midyear we realized that we first needed to develop methods to utilize seismic histories at the outer boundaries of the numerical grid. Our initial numerical results were used in a proposal

submitted to the National Science Foundation.

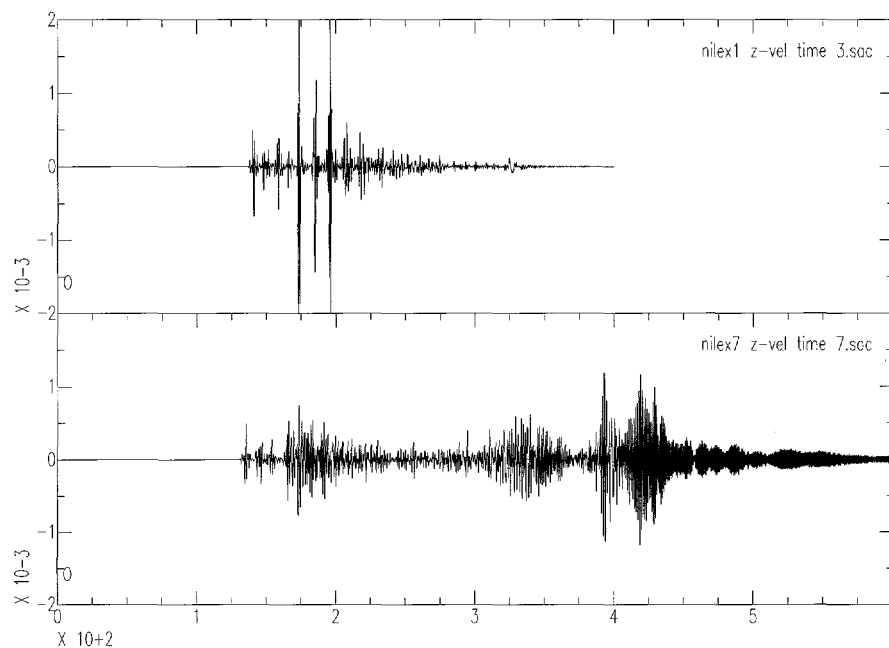
We also applied the AFD code to study path effects on seismic signals in Western China, and we completed a parameter study to isolate the effects of major geologic features along the path, such as the Tarim Basin and the Moho root of the Himalayas (see diagram of the major geologic features in this region). As shown the accompanying vertical-velocity seismograms, the low-velocity basin is particularly effective in converting compressive (P-wave) energy from an explosive source into the shear wave (S-wave) energy characteristic of an earthquake.



Three-component synthetic seismograms showing the diagonal (xx, yy, zz) components of the moment tensor, observed 450 km from a source 50 km deep in a subducting slab with a 10% velocity contrast. For each component, the bold line is a finite-difference result for the case with the subducting slab, and the dashed line is for the "no-slab" case. Z, R, and T correspond to vertical, radial, and tangential displacements. Differences in phase and amplitude for the slab and no-slab cases indicate that standard, flat-layer analysis techniques of the synthetic seismograms would produce inaccurate source characterizations.



The geologic structures along a path from the Chinese nuclear test site at Lop Nor (left) to a seismic station in northern Pakistan (right). The major features include the low-velocity Tarim Basin, which lies between 100 and 400 km from Lop Nor, and the deep Moho depression underneath the Tibetan Plateau from 1100 km to the right side of the computational region.



Vertical-velocity seismogram at $x = 1100$ km for a case not including (top) and including (bottom) the Tarim Basin. In the upper portion of the figure, the first arrival from an explosive source is at about 140 seconds and is a compressive wave which travels mostly through the high-velocity mantle material. Arrivals starting at 190 seconds represent compressive energy ducted in the crust. In the lower portion of the figure, the arrivals between 200 and 225 seconds represent compressive-to-shear (P-S) energy conversion at the upward sloping edge of the basin between $x = 600$ km and $x = 1000$ km, and the arrivals between 340 and 360 seconds represent P-S conversions on the downward slope of the basin between $x = 100$ and $x = 500$. The large-amplitude arrivals after 400 seconds represent surface waves created in the basin. In a simpler geologic setting, the shear-wave arrivals would be characteristic of an earthquake source and not an explosive source.

Lead Immobilization in Thermally Remediated Soils and Igneous Rocks

Donald D. Hickmott

Cleanup of rocks, soils, and aquifers contaminated with mixtures of lead and organic or high-explosive wastes is a problem of considerable importance across the nation. This project is designed to (1) investigate the speciation of lead in soils and igneous rocks; (2) use numerical techniques to investigate phases that may immobilize lead; and (3) perform laboratory-scale experiments in which lead is immobilized by thermal treatment of soils. Our project will result in an understanding of factors that control whether the mobility of lead in soil can be minimized by thermal treatments.

In this review period we have successfully identified lead phosphates as the most likely phases suitable for using thermal-treatment

methods to immobilize lead. We modeled the thermodynamics and kinetics of the precipitation of lead immobilizers at both ambient and high temperatures. Experiments determined that Na_2HPO_4 amendment of lead chloride can produce lead phosphates at high temperatures (400°C) but that lead carbonate and lead oxide are stable relative to lead phosphate in most bulk compositions at the temperatures investigated.

Clearly, kinetic factors influence our ability to produce thermodynamically stable, lead-phosphate-bearing assemblages in thermal remediation experiments. Further investigation of the dissolution/precipitation kinetics of lead-immobilizing phases is required before thermal immobilization of metals in soils can be implemented on a wide scale.

Publications

Eppler, A.S., D.A. Cremers, D.D. Hickmott, et al., "Matrix Effects in the Detection of Pb and Ba in Soils using LIBS," *Appl. Spectrosc.* **50**, 1175 (1996).

Hickmott, D.D., J.M. Herrin, R.A. Abell, et al., "Environmental Applications of Nuclear Microprobes" (submitted to *Nucl. Instrum. Phys. Res. B*).

Larocque, A.C.L., C.E. Chapin, et al., "Metal-Residence Sites in Mine Tailings in the Magdalena District, New Mexico," in *Mineral Deposits*, Pasava, Kribek, and Zak, Eds., (A.A. Balkema, Rotterdam, Netherlands, 1995), pp. 661-664.

Stimac, J.A., D.D. Hickmott, R.A. Abell, et al., "Redistribution of Pb and Other Volatile Trace Metals during Eruption," *J. Volcanol. Geotherm. Res.* **73**, 245 (1996).

Experimental Studies of Auroral-Arc Generators

David Suszcynsky

The focus of our project was the preliminary analysis of all-sky and satellite data and the identification of phenomena/events for future studies. We completed two analyses. The first was a survey of the satellite and ground data to identify signatures of discrete auroral arcs at geosynchronous orbit. The second analysis characterized the geosynchronous environment during pulsating aurora and black-aurora events.

In the effort to identify signatures of discrete auroral arcs, we discovered that although specific conditions at geosynchronous orbit could be associated with the occurrence of

general discrete arc activity, no specific features in orbit could be associated with individual arc structures. This information leads us to conclude that the fine structure of discrete arcs is generated at lower altitudes than the equatorial magnetosphere.

In characterizing the geosynchronous environment during pulsating aurora and black-aurora events, we learned that the geosynchronous orbit is dominated by electron pitch-angle anisotropies (pancake distributions) and fluxes, as predicted by leading pulsation theories. As expected, we observed that the pulsations occurred

during the recovery phase of substorms and often became re-energized during the growth phase of successive substorms. This observation supported the idea that the precipitating particles are supplied directly by injection events. We found that a black aurora, a rarely observed and studied phenomenon, was associated with counterstreaming 0.2- to 2-keV ions and is much more common than previously reported.

Publications

Suszcynsky, D.M., J.E. Borovsky, et al., "Coordinated Ground-Based and Geosynchronous Satellite-Based Measurements of Auroral Pulsations" (Twenty-third Conference on Optical Methods for Atmospheric Research, Kiev, Ukraine, September 2-6, 1996).

Fundamentals of Laser Ablation in the Analysis of Geological Materials

Aaron Koskelo

Our goal is to determine the parameters that contribute to matrix effects in laser ablation of materials. Laser ablation underlies many of the methods that hold promise for real-time materials recognition and rapid chemical analyses of environmental samples. However, laser ablation has not yet gained widespread use as a method of analysis nor regulatory acceptance because of matrix effects. Different sample types exhibit different sensitivities under laser ablation. This effect arises from the complex and not-yet-understood ablation process itself, particularly in mixed or inhomogeneous materials. We are developing new techniques to examine the causes of the difference in sensitivity of different materials, with particular emphasis on fundamental measurements of processes involved in the laser ablation of geological materials and soils

This year we developed the use of correlations in laser-induced breakdown spectroscopy (LIBS) spectra to examine the inhomogeneity of soils and mine tailings. We obtained a series of single-shot LIBS spectra and calculated interwavelength correlation matrices that reveal the correlation between different species emitting in the laser ablation plume. The work reveals that some Resource Conservation and Recovery Act (RCRA) metals correlate well with iron-containing components of the soil matrix but not with titanium components.

We have also seen indications that atomic and ionic lines in the laser ablation plume are anticorrelated, as shown in the accompanying figure. Strong correlation to the titanium ion emission line at 3360.96 Å occurs for every ionic line in this emission spectrum. Every atomic line in the spectrum—regardless of atomic species from which the line originates—exhibits anticorrelation to

the ionic line. This effect is explained by a shot-to-shot change in electron density in the plume. There are also indications that the degree of anti-correlation depends on how easily the element is ionized.

This year we also gained experience in the use of infrared pump-probe technology for monitoring bond breaking in materials. We expect to extend this technology to use in complex materials like geological materials.

We studied the photodecomposition of diazo-Meldrum's acid in a polymethyl methacrylate (PMMA) matrix and found that the intermediate keto-ketene appeared within 20 ps of the photoexcitation. This work indicates that the path through the keto-ketene is the primary reaction pathway to the stable carboxylic acid. It is the carboxylic acid that makes this system useful for base-soluble photoresists.

Publications

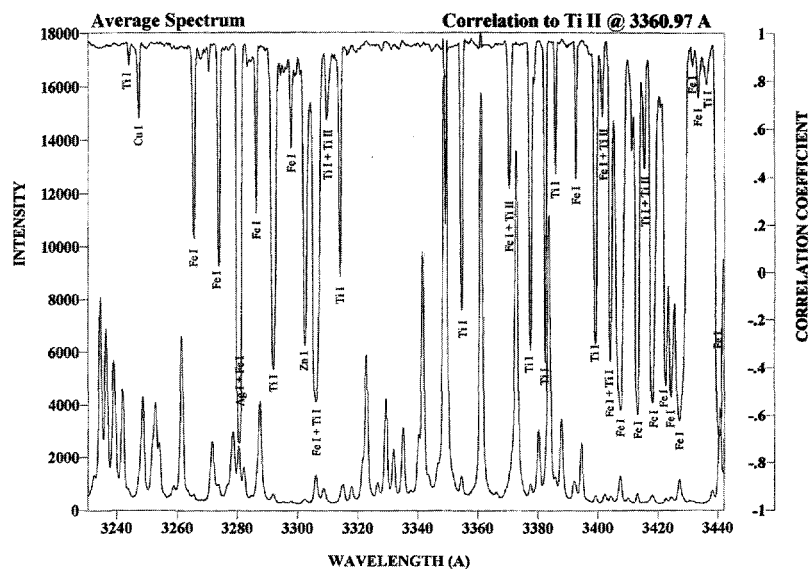
Koskelo, A., and T. Gamble, "Laser Ablation of Geological Materials" (Federation of Analytical Chemistry and Spectroscopy Society, October 1996).

Koskelo, A., T. Gamble, and T. Lippert, "Laser Induced Breakdown Spectroscopy of Geological Materials" (Winter Conference on Plasma Spectroscopy, January 1996).

Koskelo, A., C. Mahan, et al., "Direct Chemical Analysis at Los Alamos National Laboratory (SPIE National Meeting, Denver, Colo., August 1996).

Lippert, T., A. Koskelo, and P. Stoutland, "Direct Observation of a Photoinduced Wolff Rearrangement in PMMA Using Ultrafast Infrared Spectroscopy," *J. Am. Chem. Soc.* **118**, 1551 (1996).

Lippert, T., A. Koskelo, and P. Stoutland, "Laser-induced Reactions in a Deep UV Resist System: Studied with Picosecond Infrared Spectroscopy," *Mater. Res. Soc. Proc.* **397**, 661 (1996).



Correlation spectrum obtained from a sample of mine tailings from Butte, Montana. The spectrum shown is the average of 910 spectra taken as the sample moved continuously under repetitive laser sparks. Each data point is the correlation coefficient of the wavelength channel to that of a channel corresponding to Ti(II) emission. Note the strong correlation to Ti(II) for all other Ti(II) lines. Atomic emission lines do not have a strong correlation to the Ti(II) lines and, indeed, do exhibit some anticorrelation.

Integrating Chemistry into Three-Dimensional Climate Models: Detailed Kinetics in the Troposphere and Stratosphere of a Global Climate Model

Chih-Yue J. Kao

Several atmospheric gases, including ozone and methane, are both radiatively and kinetically active. They influence global climate but are themselves controlled by photochemical processes. The role of such molecules in the global system has generally been simulated either in low dimensionality or with chemistry decoupled from dynamics. Three-dimensional chemical models have further sacrificed integrity by focusing either above or below the tropopause.

The goal of our research is to alleviate these restrictions by incorporating kinetics interactively into both the troposphere and stratosphere of a global climate model (GCM) so that the chemical and thermodynamic effects of important atmospheric gases can be comprehensively modeled and used by decision-makers in coping with the changing earth-atmosphere system. We expect to create the first truly interactive, three-dimensional, chemical climate simulations. Our work on this project has applications to photochemistry, environmental sciences, chemical transport, and monitoring.

This year we implemented the parameterization of aerosol formation and chemical heterogeneous reactions in our photochemical module to study the influence of aerosol on ozone concentrations. In particular, we investigated the heterogeneous chemistry occurring on the sulfate particles from volcanic eruptions. We compared the simulated ozone depletions with documented data from eruptions such as El Chichon and Pinatubo.

Publications

Elliott, S., C.-Y.J. Kao, F. Gifford, et al., "Free Troposphere Ozone Production after Deep Convection of Dispersing Tropical Urban Plumes" (to be published in *Atmos. Environ.*).

Elliott, S., M. Shen, C.-Y.J. Kao, et al., "A Streamlined Family Photochemistry Module Reproduces Major Nonlinearities in the Global Tropospheric Ozone System," *J. Comput. Chem.* **20**, 235-259 (1996).

Zhao, X., R.P. Turco, et al., "Aerosol Induced Chemical Perturbations of Stratospheric Ozone: Three-Dimensional Simulation and Analysis of Mechanisms" (submitted to *J. Geophys. Res.*).

Zhao, X., R.P. Turco, et al., "Numerical Simulation of Dynamical Response to the Arctic Vortex to Aerosol-Associated Chemical Perturbations in the Lower Stratosphere," *Geophys. Res. Lett.* **12**, 1525-1528 (1996).

Using Microspheres as Tracers for Flow in Geologic Media

Bruce A. Robinson

The goal of this study is to develop microspheres as groundwater tracers. This capability will allow us to investigate the movement of colloidal contaminants in groundwater and to gain insight into the movement of dissolved and colloidal contaminants in fractured rock. We used polystyrene latex and silica microspheres (0.25 to 1 μm in diameter) tagged with fluorescent dyes in laboratory and field groundwater-tracer experiments to (1) obtain insights into colloidal contaminant transport in geohydrologic systems, and (2) characterize geohydrologic systems more thoroughly than we could using only dissolved tracers.

We have measured microsphere concentrations in groundwater samples at two to three orders of magnitude below natural background concentrations, using the unique capabilities of the flow cytometry laboratory at Los Alamos. Preliminary results suggest that the use of microspheres in tracer experiments can provide valuable insights into

colloid-transport mechanisms and retardation/attenuation mechanisms of solute contaminants in saturated groundwater systems. Laboratory experiments revealed that negatively charged, carboxylate-modified microspheres provided the most mobile surface-charge characteristics in natural groundwater systems. Field studies of fractured granite supported our theory that microspheres travel slightly faster than dissolved tracers in forced-gradient tests. However, attenuation, possibly caused by settling, also affects the field results.

This work has resulted in several master's and doctoral theses at two universities.

Publications

Reimus, P.W., B.A. Robinson, et al., "Simultaneous Transport of Synthetic Colloids and a Nonsorbing Solute through Saturated Rock Fractures," *Mat. Res. Soc. Symp. Proc.* **353**, 363-370 (1995).

Theoretical Research on Dwarf and Classical Novae

Warren Sparks

Previous simulations of accreting white dwarfs (WDs) have been one-dimensional. The recent identification of the two-dimensional (2-D) belt structure on the WD surface in VW Hyi demands more realistic simulations using a 2-D model, which we are developing. To allow the model to have time steps exceeding the limit set by the Courant condition (the sound-crossing time in a grid cell inside the degenerate WD), the code has to be implicit for numerical stability. Using an energy criterion of shear mixing characterized by the Richardson number, we find that the forced convection is most efficient along the equipotential surface of the differentially rotating WD atmosphere. To

simulate this effect, we developed a new time-dependent zoning scheme in which the time-dependent grid follows the equipotential surfaces.

The standard alpha-model theory predicts that during a dwarf nova outburst, the boundary layer between the WD surface and the inner disk radiates away one-half of the accreted energy from a small area of the WD stellar surface and has an effective temperature as high as 500,000 K. Recent observations show that during a dwarf nova outburst, a significant portion of the gravitational energy accreted onto the WD may not be radiated away instantly from a narrow boundary layer as predicted by the standard disk theory. In collaboration

with Villanova University, we have found various means of transporting this energy deeper into the star and extending the radiative region. Thus, we may account for the long-puzzling missing boundary layer when we consider the response of the WD to the accretion.

In collaboration with the University of Wyoming, we investigated the cause of the high and low accretion states in AM Herculis binaries (AM Hers). We proposed a model in which the WD's rotation acts like an angular momentum storage battery for the binary orbit. The accreted material from the Roche lobe—overflowing secondary charges up this battery, whereas the magnetic torque of the WD on the secondary discharges it back into the binary's orbit. The Roche lobe's volume becomes alternately larger and smaller than the secondary's volume. This alternation causes the mass flow to vary between a high and low rate.

Micro/Macroscale Coupling in Magnetospheric Plasmas

S. Peter Gary

Microscale plasma processes can significantly affect the large-scale dynamics of a plasma, whereas large-scale computer models of space plasmas cannot directly model kinetic process and require special algorithms to adequately represent small-scale effects. Our goal is to develop new scaling relations for proton parameters that allow good quantitative representation of the consequences of microphysical processes that take place in the magnetosphere.

We have recently developed the first scaling relation for the hot-proton-anisotropy upper bound in magnetospheric plasmas and have used it as an algorithm in a computer model of the magnetotail to demonstrate that it qualitatively affects the predictions of that model. We are

using plasma theory, hybrid simulations, and spacecraft data analysis to develop additional new scaling relations for the consequences of small-scale instabilities in the magnetosphere. These relationships significantly improve the predictive capabilities of the models.

We have recently published two important results. The first, which was obtained through the use of two-dimensional computer simulations, is that the whistler anisotropy instability imposes an upper bound on the temperature anisotropy of electrons that have bi-Maxwellian velocity distributions. This result is fully analogous with the upper bound we have demonstrated for ion temperature anisotropies. The second important result is that the scaling relation

for the properties of anisotropic protons near 10 eV (i.e., "warm" protons) in the outer magnetosphere provides an approximate upper bound for a selected set of warm-proton temperatures observed at geosynchronous orbit.

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Numerical Simulations of Convection Experiments and Earth's Interior

Gary Glatzmaier

Our project is targeted at providing new insights and explanations about the origin, structure, and evolution of Earth's magnetic field through the development of a dynamically consistent, three-dimensional computer model of the geodynamo—the convective mechanism in Earth's outer fluid core that generates and maintains the geomagnetic field. We have successfully developed the first such model and have used it in a simulation that has maintained an Earth-like magnetic field for a simulation length of more than 200,000 years.

Our simulated magnetic field has an intensity and a dipole-dominated structure that are very similar to Earth's (see accompanying figure). Our simulation also has a westward drift of about 0.2 degrees/year of the nondipolar structures of the field at the core-mantle boundary; this drift is similar to that measured on Earth. In our simulation, the solid inner core rotates about 2 to 3 degrees/year faster than the mantle. This prediction

we made for the core's rotation was recently supported by two independent seismic analyses. The radius of the inner core grows at about 3 cm per century as iron in the fluid alloy above freezes onto the core. If one assumes the heat flow out of Earth's core has remained relatively constant, the simulated growth rate implies that the age of the solid inner core is only about one-fourth the age of Earth.

In the past year, we also conducted computer simulations of the geophysical fluid-flow cell experiment that was flown aboard the NASA space shuttle *Columbia* in November 1995. This experiment will improve our understanding of convection in rotating planetary interiors.

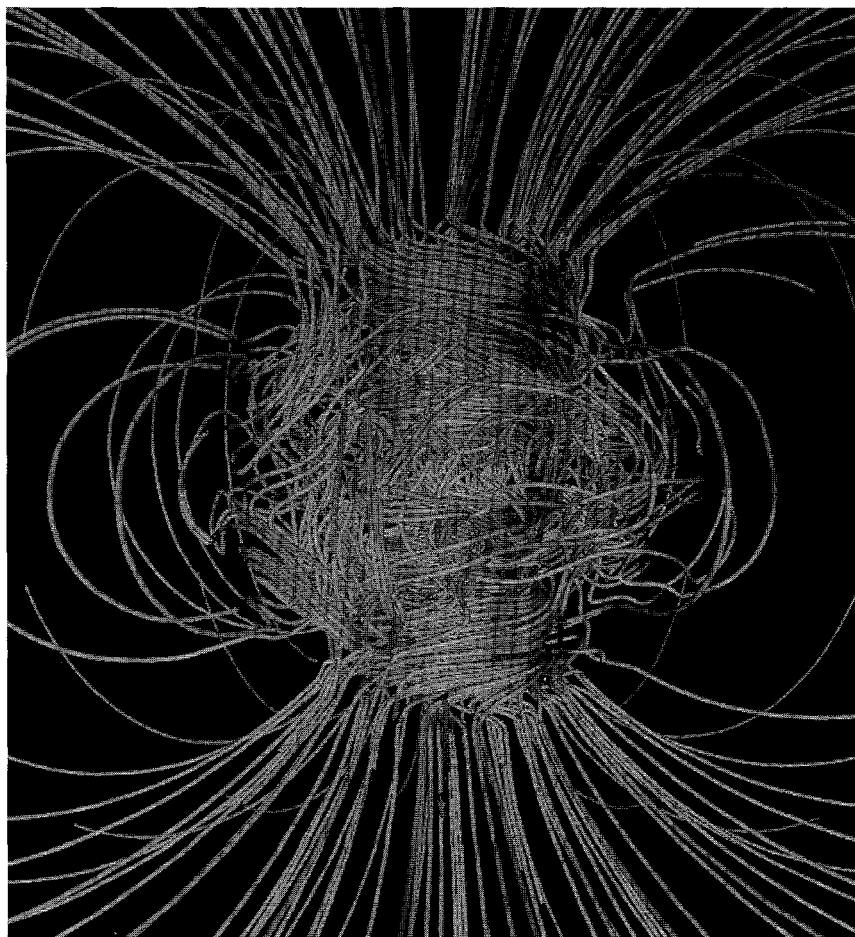
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A snapshot of the computer-simulated geomagnetic field. Magnetic field lines are drawn out to two Earth radii. The complicated intense field occurs in the fluid outer core where the field is generated; the field outside the outer core is a smooth potential field. The axis of rotation is vertical in this image.



High-Velocity Neutron Stars

Edward Fenimore

The following three recent discoveries could revolutionize our understanding of high-energy astrophysical transients: many neutron stars have sufficient velocity to escape the galaxy; soft gamma repeaters (SGRs) come from high-velocity neutron stars; and one high-velocity neutron star may have produced a gamma-ray burst. Our project goal is to understand these phenomena and determine under what conditions the observed high-velocity neutron-star properties (when applied to the local group of galaxies) can reproduce all of the properties of high-energy transients;

namely, an apparent isotropic distribution and uniform density of gamma-ray bursts, a lack of events from the Andromeda Galaxy, the association of SGRs with population I material, and the fact that a young neutron star was able to produce both SGRs and gamma-ray bursts.

During this year we completed three steps in understanding gamma-ray bursts from galactic high-velocity neutron stars. First, since the March 5th burst event (which was the brightest event ever observed), we have searched for fainter versions that might have come from nearby

galaxies. For example, the Burst and Transient Source Experiment can observe March 5th-like bursts out to 5 Mpc, a volume that contains 70 galaxies. No events were found, showing that they are less frequent than the rate seen in our galactic neighborhood.

Second, we investigated what would be necessary to detect gamma-ray bursts from the Andromeda Galaxy in anticipation of possible NASA gamma-ray-burst satellites that would attempt to detect bursts from Andromeda. We published an analysis based on our models of high-velocity neutron stars, which showed that only one class of models can be tested with a next-generation satellite (the "delayed turn-on" models), whereas the other models (based on beaming) cannot be tested.

Third, we evaluated what relativistic motion would be required to allow the escape of the observed very high energy photons from a neutron star. We found that much slower relativistic motion could be present (Lorentz factors of only 5 rather than 50). The slower motion will allow a wider range of high-velocity neutron-star models.

Sedimentary Basin Response to Strong Motion in Populous Regions

Paul Johnson

An important origin of damage in modern metropolitan areas during large earthquakes is the amplification of seismic shear waves. The amplification is due to both basin-geometry-induced resonance and local site resonances. Examples of amplification include all of the most damaging earthquakes of the latest decade, including the 1985 Michoacan (Mexico), the 1989 Loma Prieta (California), the 1994 Northridge (California), and the 1995 Kobe (Japan) earthquakes. These earthquakes cost thousands of lives, mostly resulting from structural failure, and cost tens of billions of dollars in structural damage. Consequently, understanding and mitigating the effect of the uppermost sedimentary layers on ground motion and the resulting response of engineered structures is of paramount importance.

In the past year, we focused primarily on obtaining high-quality,

strong-motion data from the main shock and aftershocks of the Northridge earthquake to study site effects. Our preliminary analysis shows strong nonlinear-induced resonance changes at several strong-motion sites in the Los Angeles basin. A three-day conference at Los Alamos regarding preliminary progress was held in September 1996 with all project participants. An exhaustive analysis of all strong-motion sites has begun as a result of observations and discussions.

Simultaneously, we began working with groups that are creating whole-basin, finite-element difference models of the Los Angeles basin. We will incorporate observations and nonlinear response models being developed at Los Alamos into basin models. We also recently obtained data, for additional studies, on the Kobe earthquake and on several earthquakes in Taiwan.

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Heterogeneous Processing of Bromine Compounds by Atmospheric Aerosols: Relation to the Ozone Budget

Jeanne M. Robinson

In this project we have studied the adsorption of halogenated gases on ice aerosols and the potential contribution to ozone depletion. Before the discovery of the "ozone hole," these heterogeneous processes were ignored in atmospheric chemistry models. Field measurements supported by laboratory experiments and modeling have confirmed the pivotal role of reactions of photoinactive (reservoir) chlorine and nitrogen gases on ice and nitric acid ice aerosols in the Antarctic polar vortex. It was subsequently recognized that heterogeneous processing on the background sulfuric acid aerosols distributed worldwide at mid-latitudes presented a potential threat for global ozone depletion.

Attention is now turning to bromine compounds that undergo the analo-

gous reactions and likely play a significant role in ozone depletion in the Arctic boundary layer. We use a nonlinear optical probe, second harmonic generation (SHG), to measure the thermodynamic behavior of porous ice films and adsorption of bromine compounds on the ice. Our formalism allows us to measure the adsorption isotherm for an adsorbate/ice system and quantify the adsorption on these heterogeneous substrates in terms of the multilayer structure and adsorbate coverage. We have used SHG to measure the uptake of HBr by water ice at low temperatures and to monitor the phase behavior of HBr hydrates as a function of temperature. The adsorption isotherm shown here resembles our results for HCl adsorption at slow introduction rates.

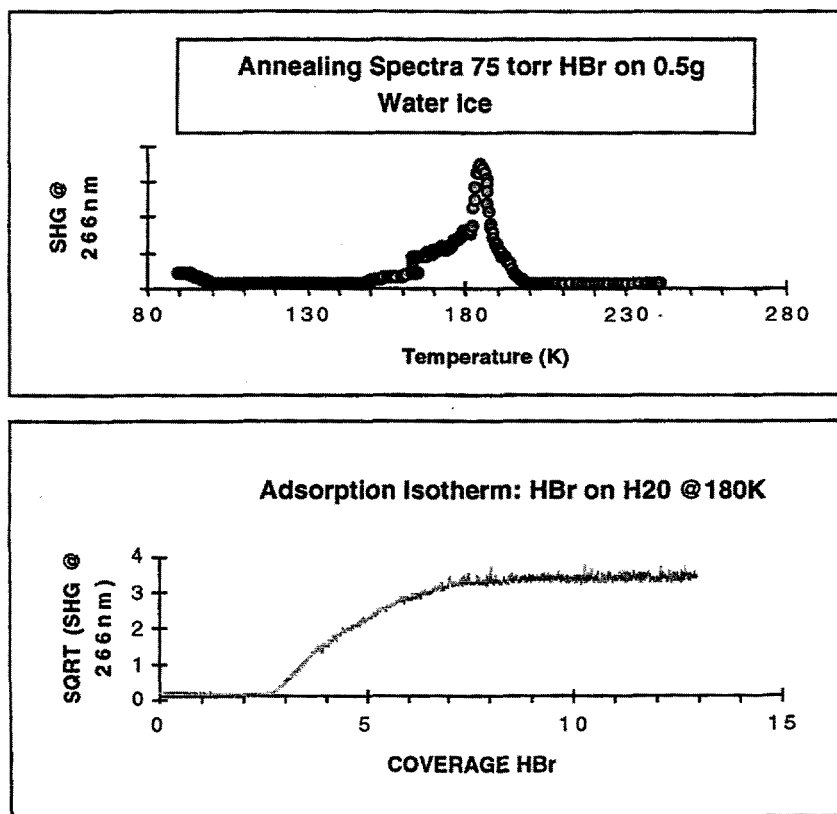
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HBr adsorption into a porous water ice substrate. The upper panel shows the SHG intensity as a function of temperature for a water ice with 0.7 monolayers HBr adsorbed. The lower panel shows an adsorption isotherm for HBr at 180 K, which can be analyzed using Brunauer-Emmett-Teller multilayer adsorption theory.

Coronal Mass Ejections in the Solar Wind

John Gosling

Coronal mass ejections (CMEs) are spectacular solar events in which large amounts of material from the solar atmosphere are ejected into interplanetary space. The processes that trigger the release of CMEs from the sun and the factors that determine their sizes, their speeds, and their evolution in interplanetary space are only poorly understood. In this project we are studying CMEs in the solar wind near Earth's orbit.

Our overall goals are to distinguish and understand the physical processes governing CME evolution in interplanetary space and to learn how best to identify CMEs in solar wind plasma and magnetic field data. Of particular interest is investigating the role that three-dimensional (3-D) magnetic reconnection plays in determining the overall magnetic topology of these vital interplanetary objects. We are analyzing and interpreting solar wind plasma and magnetic field data archived at Los Alamos from a variety of space probes.

Our review of transient solar wind flows showed that 3-D reconnection provides a logical framework for explaining a diverse set of solar and solar wind observations related to CMEs. One new insight is that it is the plasma beta (ratio of plasma to magnetic pressures) within a CME that determines if 3-D reconnection will produce the nearly force-free structure characteristic of "magnetic clouds," which form an important subset (about one-third) of all CMEs observed in the solar wind near Earth's orbit.

We also found that ~20% of all CMEs previously identified in the solar wind near Earth contain either open or completely disconnected magnetic field lines, suggesting the presence of sustained 3-D reconnection in at least these events. Our preliminary calculations show that the forces associated with rarefactions produced in front of slow CMEs are insufficient to explain observed accelerations of such CMEs in the solar wind.

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Modeling Core-Collapse Supernovae in Three Dimensions

Michael Warren

The deaths of massive stars in supernova explosions are the most violent events ever witnessed by human beings. As a consequence, understanding core-collapse supernovae represents a fascinating challenge which requires the convergence of such varied areas of expertise as nuclear physics, neutrino transport, and hydrodynamics. In addition, the extreme conditions of density, temperature, and gravity which reign

at the heart of supernovae make them a natural laboratory in which to test ideas about physics that are otherwise difficult to investigate on Earth.

We have previously established that the mechanism which powers supernova explosions relies on large-scale convection driven by neutrino heating. However, determining the pattern of this convection demands three-dimensional simulations, which have not yet been performed. Using

our combined expertise in parallel computing and supernovae theory, we are beginning to carry out such simulations. We will then use the results to estimate the kick velocity imparted to neutron stars at birth, which has far-reaching implications for models of gamma-ray burst sources. We have thus far extended an existing parallel, smooth-particle hydrodynamics code into a full-fledged supernova code. We have also begun developing a parallel, multidimensional, mesh-refined, shock-capturing method that should provide significantly improved simulation capability.

Deriving the Structure of Presupernovae and Delta Scuti Stars Using Nonradial Oscillations

Joyce Guzik

We are modeling the evolution and pulsation of luminous blue variables (LBVs) and delta Scuti stars. The LBVs are massive stars and Type II supernova progenitors, while the delta Scuti variables are slightly more massive than the sun. Both types of stars pulsate in multiple radial and nonradial modes that have significant amplitudes throughout the stellar interior. We are improving the model physics and comparing predicted and observed pulsation properties to constrain the interior structure of these stars (see the first figure). The study of stellar interiors can contribute to the understanding of fundamental physics, such as equations of state (EOSs) and opacities of dense plasmas, energy transport, and turbulent mixing.

This year we updated and are now using a nonlinear hydrodynamics code to determine whether predicted radial "strange" modes can grow to large amplitude and trigger LBV outbursts (see the second figure). We compared observed and calculated oscillation frequencies to derive stellar parameters for two delta Scuti stars, FG Vir and CD-24° 7599 (see the third figure). We participated in a very successful multisite observing campaign for the delta Scuti star 4 CVn, which resulted in detection of over 30 new frequencies.

In addition, we modified a two-dimensional stellar evolution code to handle convective envelopes present in lower-mass stars and benchmarked this code by calculating a rotating, two-dimensional solar evolution model. We used the hydrodynamic capabilities of this code to look for rotation-generated shear instabilities

and possible turbulent mixing below the solar convection zone. We are applying this code to model the more rapidly rotating delta Scuti stars.

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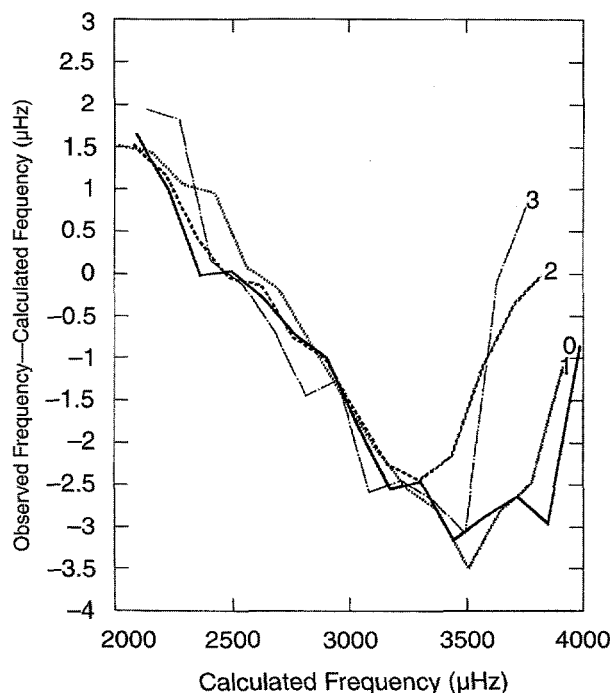
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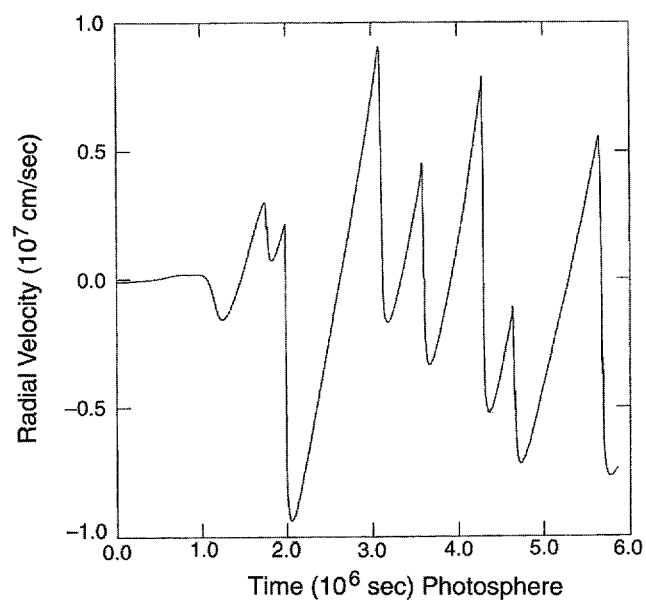
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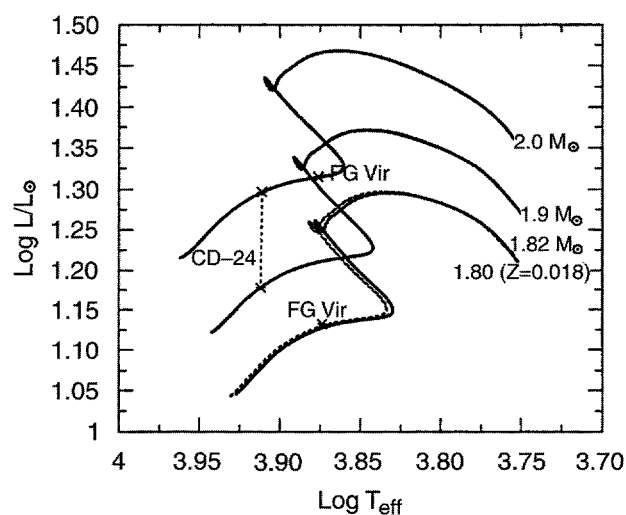
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The discrepancy between observed and calculated solar oscillation frequencies vs calculated frequency for the low-degree (0, 1, 2, and 3) acoustic waves that travel through most of the solar interior. The solar model includes diffusive settling of helium and heavier elements relative to hydrogen and uses the latest opacity-library (OPAL) opacities and an analytical EOS developed by F. Swenson (Los Alamos), F. Rogers (Lawrence Livermore National Laboratory), and A. Irwin. We can eliminate the remaining small discrepancy between observed and calculated frequencies by refining the solar surface modeling.



Growth in surface radial velocity from hydrodynamic calculation of the LBV envelope model. This model represents a star of initial mass equal to 80 solar masses that has lost nearly half its mass because of an intense stellar wind, exposing layers where 50% of the original hydrogen has been converted to helium by nuclear fusion. Linear pulsation analysis shows that this model is unstable to radial “strange” mode pulsations. The model predicts that the kinetic energy of two modes, with periods of 7 and 15 days, more than doubles each period. Nonlinear analysis shows that for this model, the pulsation amplitude grows to about 100 km/sec (only about 1/3 escape velocity) before reaching a limiting amplitude.



Location in the Hertzsprung-Russell diagram (the log of the luminosity vs the log of the surface temperature) of best-fitting models for the delta Scuti stars FG Vir and CD-24° 7599, along with evolution tracks for 1.8, 1.9, and 2.0 solar mass models. Models of 1.9–2.0 solar masses and effective temperature 8200 K match most of the 13 reported oscillation frequencies of CD-24° 7599. Models with effective temperature 7480 K, of either 1.8 or 2.0 solar masses, best match the 19 reported frequencies for FG Vir.

Magmatic Tritium

Fraser Goff

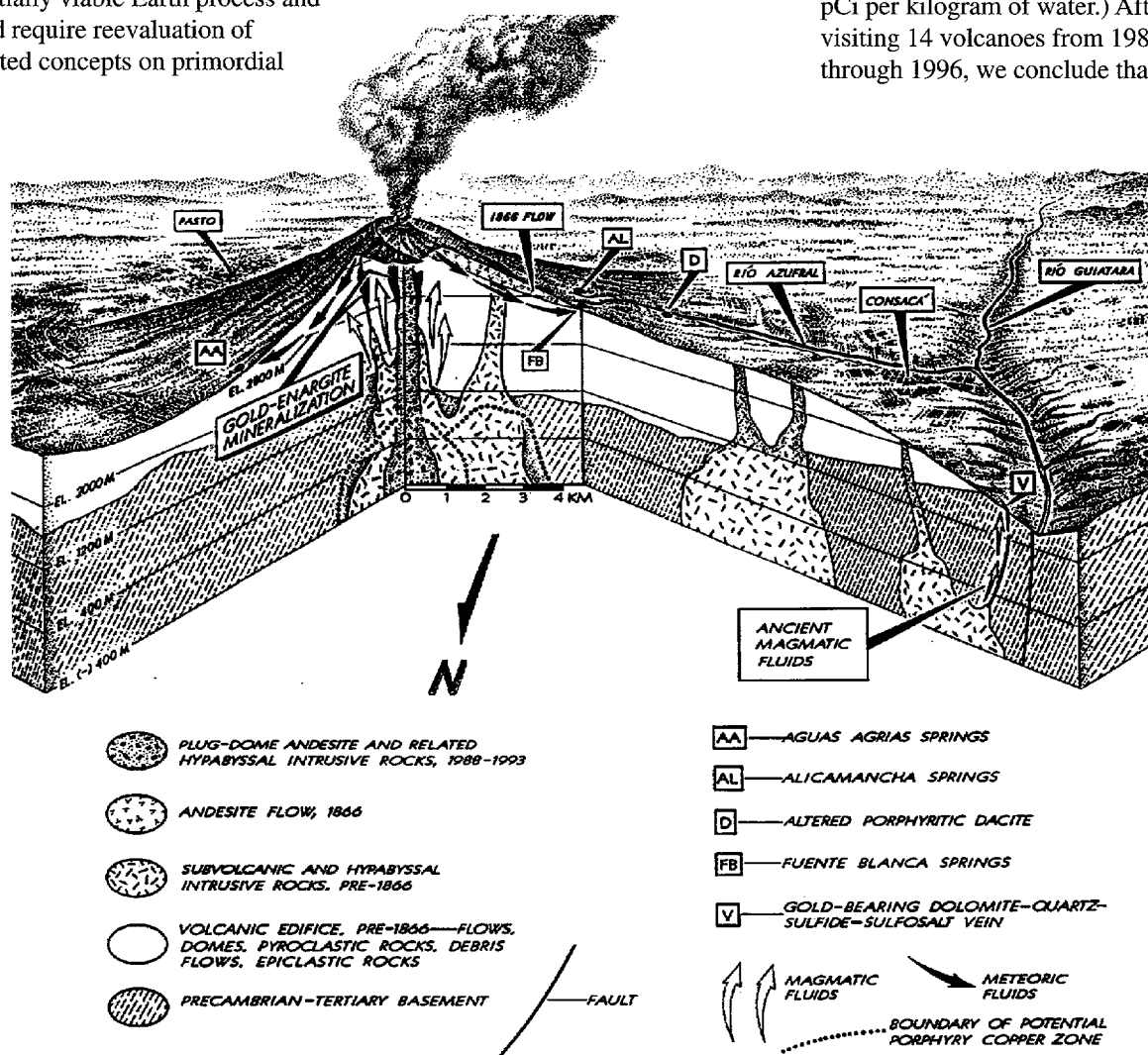
Tritium (^3H) is one of the reaction products that should be produced during "cold fusion" in condensed matter. We are trying to determine whether anomalous quantities of tritium are universally present in magmatic waters from several volcanoes of different magma types and tectonic settings. The presence of such tritium could provide independent evidence for cold fusion as a potentially viable Earth process and would require reevaluation of accepted concepts on primordial

helium, mantle heat flow, and plate tectonics.

The object of our work is to collect samples of high-temperature fumarole condensates, thermal and nonthermal groundwaters, precipitation, and fresh volcanic products from one additional volcano to determine the tritium content of its magmatic water. Our approach is unique because we analyze water with three isotopic

compositions (water containing deuterium, oxygen-18, and tritium) to eliminate effects of meteoric contamination and contamination by near-surface groundwaters.

Targeted volcanoes for this past year were White Island and Ruapehu (New Zealand). We have not quite completed the data analysis for the New Zealand samples, but we have completed the analyses of samples collected last year from Vulcano (Italy), Kudriav (Russia), and Panandayan (Indonesia) and found that their magmatic tritium is 0.0 tritium units (T.U.). (1 T.U. = 3.193 pCi per kilogram of water.) After visiting 14 volcanoes from 1988 through 1996, we conclude that



Modified cut-away perspective drawing (viewed from the north) of Galeras volcano, Colombia, showing the basic geology and configuration of the shallow hydrothermal system. Magmatic volatiles mix with young, near-surface groundwaters to form acid springs. Magmatic fluids discharging inside the volcano create conditions favorable for deposition of gold and copper. Magmatic fluids discharging at the summit mix with precipitation falling in the summit crater and cone. The resulting mixtures contain measurable tritium from the meteoric end-member but no detectable tritium from a deep source.

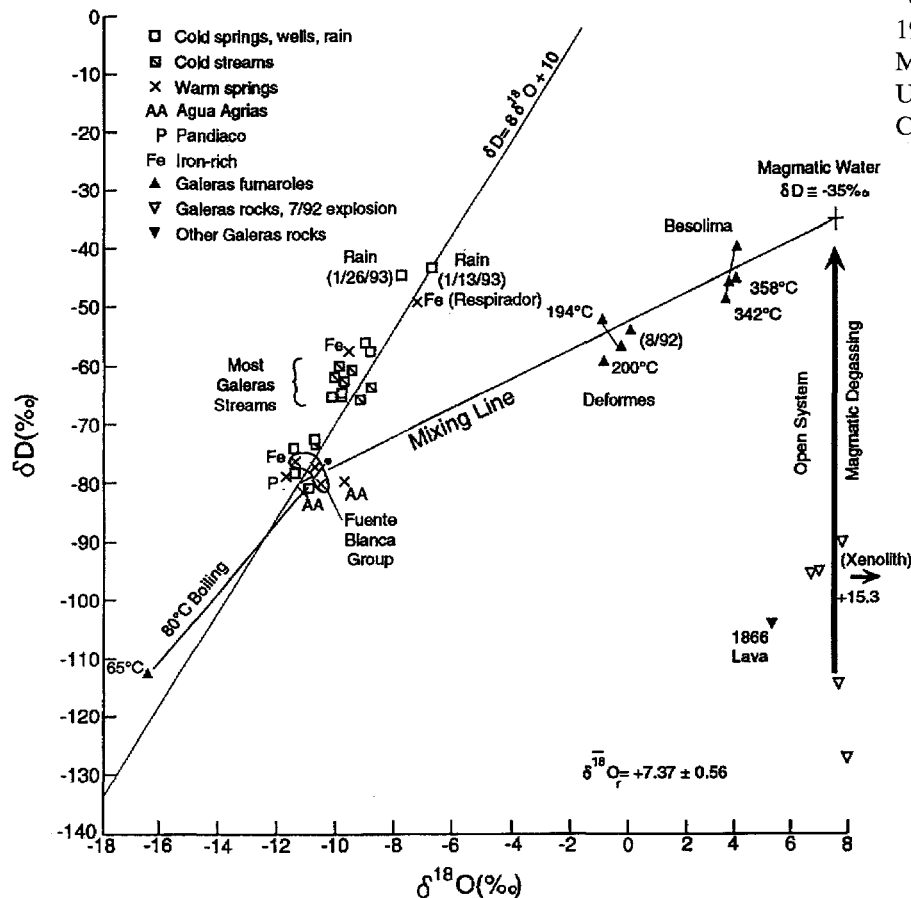
magmatic tritium is in all cases 0.0 T.U., subject to analytical and other errors. Thus, there are no identifiable magmatic tritium anomalies and no evidence for cold fusion in the deep Earth. The results of this

project also have application to studies of natural cycling of meteoric tritium and of metals transport in magmatic fluids, as well as for hazards monitoring at volcanoes.

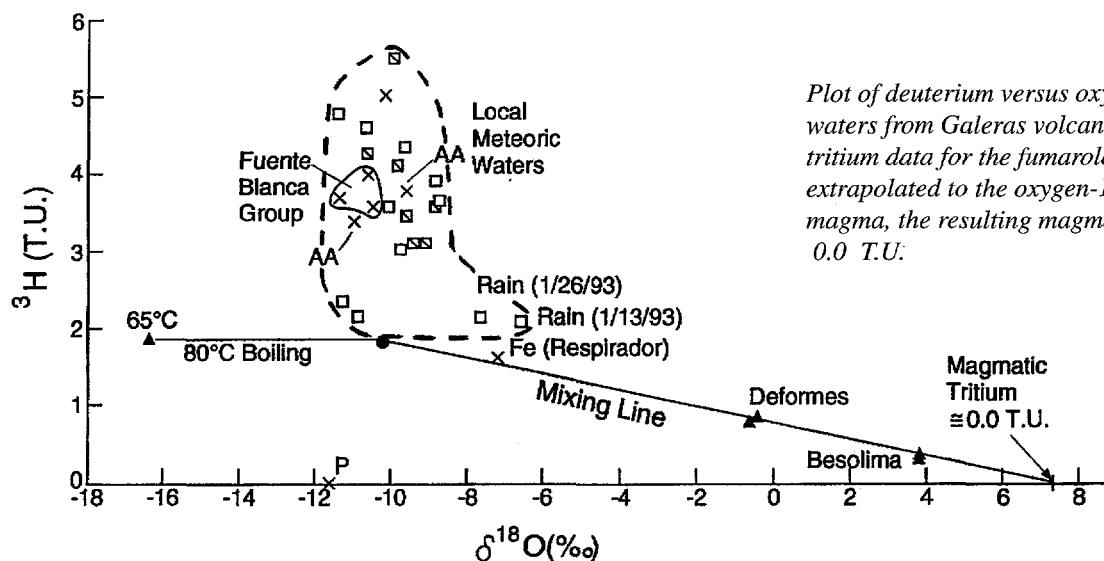
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Plot of deuterium versus oxygen-18 for waters from Galeras volcano. The fumarole condensates lie on a mixing line between magmatic and meteoric end-members. The extrapolated deuterium of the magmatic water is about -35‰.



Plot of deuterium versus oxygen-18 for waters from Galeras volcano. When the tritium data for the fumaroles are extrapolated to the oxygen-18 value for magma, the resulting magmatic tritium is 0.0 T.U.

Minerals of Earth's Deep Interior

David Schiferl

The goal of this project is to gain a fundamental understanding of the boundary between Earth's upper and lower mantle. The nature of this boundary has been a major geophysical issue for the past two decades. Specifically, we want to understand the seismic velocity and density discontinuity at the boundary, which lies at a depth of 670 km and has a temperature of about 1900 K and a pressure of about 23 GPa. A phase change at this depth would represent a relatively small barrier to mantle convection through the discontinuity, but a compositional change would inhibit thermal convection throughout the mantle.

In our project, we are measuring equation-of-state (EOS) parameters in mantle minerals as functions of high pressure and temperature using single-crystal x-ray diffraction in a unique diamond-anvil cell (DAC). Measurements are made at up to 25 GPa and 1200 K. Single-crystal

diffraction improves the absolute accuracy in lattice constants over that obtained with powder diffraction by a factor of 5 to 10.

We modified the DAC to ensure stable high pressure at high temperatures and observed seven points on the EOS of silicate perovskite. We also determined the pressure and temperature derivatives of the bulk modulus and thermal expansion for orthoenstatite (MgSiO_3) at up to 1000 K at 1.5 GPa and at lower temperatures with pressures up to 4.5 GPa (see figure). These measurements break previous records for single-crystal diffraction at high temperature and pressure and define a new state of the art.

In addition, we conducted large-volume pressure diffraction experiments at up to 10 GPa and 1300 K using a synchrotron x-ray radiation source. Experimental data on two materials, hBN and $\text{NaAlSi}_2\text{O}_6$ jadeite, have improved our understanding of

the thermoelasticities of these materials and can be applied to modeling pressure-temperature systematics and mantle mineralogy.

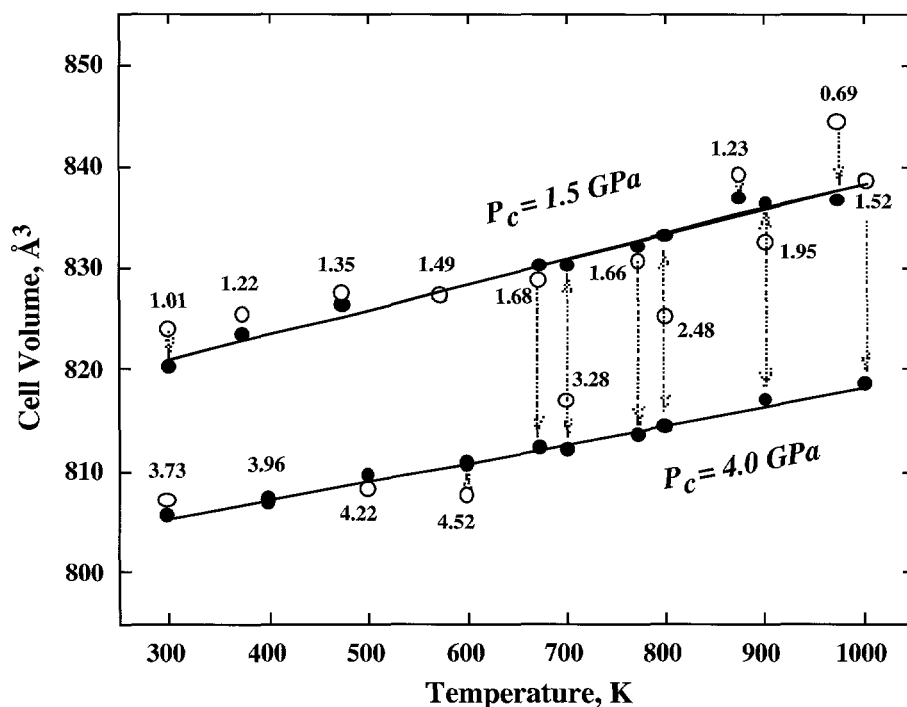
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Pressure dependence of the thermal expansion of MgSiO_3 . Open data points represent raw pressure-volume-temperature data, with their pressures labeled next to them. Solid points are corrected data (using the thermoelastic equation of state) for two constant pressures: 1.5 and 4.0 GPa. Data points between these two constant pressures are corrected twice to both pressures; the dotted arrows indicate the direction of correction. Two straight lines are fit to obtain thermal expansions at $P_c = 1.5$ and 4.0 GPa.

Striation-Image Monitoring of Plasmaspheric, L-Resolved Electrodynamics (SIMPLE)

Abram Jacobson

The plasmasphere is a region of relatively dense ionized gas in Earth's atmosphere, located in near-space within a few Earth radii in ge-altitude, that is confined by Earth's magnetic field. Our project is aimed at detecting irregularities in the plasmasphere using the electrical phase of radio signals transmitted by geosynchronous satellites, which rotate with Earth over a fixed position near the equator. The physics underlying this project is multiscale: the solar wind is the prime driver and energy source, the geomagnetic field is the intermediate store of energy from the solar wind, and Earth's ionosphere and upper atmosphere are the electrical load at the base of the geomagnetic field.

One goal of this work is to develop an entirely new approach to monitoring how Earth's near-space environment is affected by geomagnetic disturbances, which are in turn related to solar flares. This new method is potentially two orders of magnitude less expensive than existing means of monitoring near-space electric fields (such as incoherent-scatter radar and polar-orbiting satellites) during geomagnetic disturbances.

This past year has been one of enormous accomplishment and encouragement. We succeeded in tracking three satellite beacons simultaneously, significantly increasing our ability to monitor plasmaspheric irregularities. In addition, we have better defined our measurement error by examining a

subset of the data that provided a clear indicator of instrumental effects.

In addition, we firmly established that the midnight sector is the preferred site of plasmaspheric irregularities, with more day/night contrast during northern winter than during northern summer. There is a striking correlation of the intensity and incidence of these irregularities with increased levels of geomagnetic disturbance as measured by the Kp index. There is a prompt "turn-on" of the irregularities when the DST index plunges negative.

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Coupled Ocean-Atmosphere Model System for Studies of Interannual-to-Decadal Climate Variability over the North Pacific Basin

Chung-Chieng Lai

This project will improve our understanding of fluctuations in precipitation (and, therefore, water resources) in the southwestern United States. Only a coupled ocean-atmosphere model (COAM), like ours, can track the path of water from oceans through the atmosphere to land. The objectives of our project are to construct a global COAM, use the model to explore climate variability over the North Pacific basin within a period ranging from one year to

several decades, and then use the results of this study to determine the effects of climate variability in the North Pacific region on the precipitation over the Southwest.

This year, we completed three major tasks. First, we built a meso-scale COAM for the west coast by taking advantage of an existing regional atmospheric model from the University of California, Davis, and a regional ocean model from Mississippi State University. However, we still need to define a consistent set of interface boundary conditions and to

achieve temporal synchronization between the two regional models.

In the area of global modeling, we completed coupling the global ocean model constructed at Los Alamos with the global atmospheric model from the National Center for Atmospheric Research (NCAR); we also completed a one-year simulation with the global COAM. To achieve coupling of the two models, we used the "flux coupler" package developed at NCAR as part of the Climate System Modeling Project. However, we still need to improve the efficiency of the coupling process.

Finally, we designed the boundary interface for the global nested-grid ocean models in cooperation with the University of California, Los Angeles, where the North Pacific circulation model was developed and with Mississippi State, where the Gulf of Mexico model was developed.

Particle Acceleration from Reconnection in the Geomagnetic Tail

Joachim Birn

One of the major consequences of the reconfiguration of the geomagnetic field associated with magnetospheric substorms and the underlying magnetic reconnection process is the acceleration of charged particles and their injection into the ionosphere and the near-tail region of the magnetosphere. The accelerated charged particles in Earth's magnetosphere cause auroral brightening and may affect satellite safety and operations. We are investigating the mechanisms of particle acceleration and heating using self-consistent three-dimensional magnetohydrodynamic (MHD) simulations and by tracing test particles in electromagnetic fields obtained from these simulations.

New MHD results indicate a much stronger, more rapidly rising electric field in the region earthward of the reconnection site, which has important consequences for the energy gain and the increase in particle fluxes. The energetic particle flux changes estimated from the test particle orbits agree well with observations that demonstrate rapid ion-flux increases at energies above ~20 keV but little change at lower energies. The

accompanying figures show the ion flux changes and ion distribution functions during an observed particle injection and in the test particle simulation.

The "injection region" inferred from the test particles not only has a sharp earthward boundary (the usual injection boundary) but also a sharp but ragged tailward boundary. The earthward portion of the enhanced ion flux can be traced to the enhanced cross-tail electric field associated with the collapse and dipolarization of the inner tail, whereas the tailward edge is closely associated with a magnetic neutral line, the site of reconnection.

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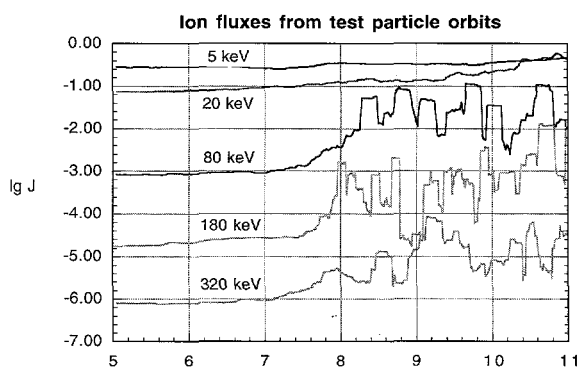
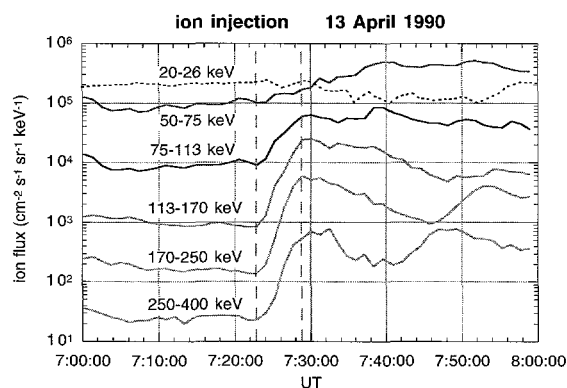
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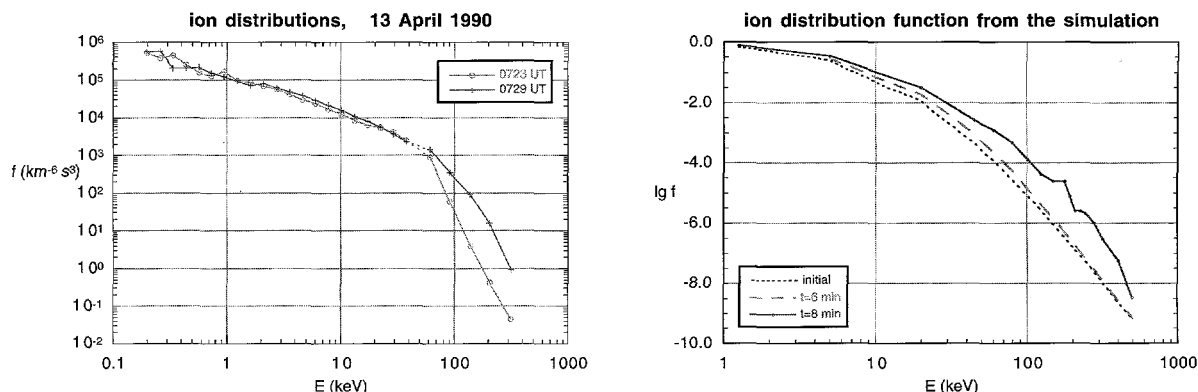


Ion flux increases observed during an injection at geosynchronous orbit (left panel) and obtained from test particle orbits integrated in the fields from an MHD simulation of the dynamic evolution of the magnetotail (right panel).

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Ion distribution functions for the previous figure; those observed during the injection (left panel) versus those calculated on the basis of the simulation (right panel).

Fluxes of Water and Energy in Physically Heterogeneous Environments

David D. Breshears

Fluxes of water and energy in the near-surface environment are tightly interrelated with the heterogeneous vegetation pattern that is a mosaic of canopies of woody plants and intercanopy areas. Our objective was to improve the predictability of these interrelationships, which are relevant to a variety of problems, including global change, land management, and contaminant transport. Using spatial autocorrelation, we demonstrated that vegetation overstory determines the patterns of soil moisture and near-ground solar radiation. The spatial pattern of soil moisture varies temporally—intercanopy patches are usually wetter than canopy patches, except after intense storms that generate runoff. We developed a water balance model that predicted the temporal shifts in soil moisture between canopy and intercanopy patches and conducted a suite of

spatial neighborhood analyses that demonstrated how trees exploit canopy/intercanopy heterogeneity. The spatial relations of trees reflect spatial variability in fluxes of water and energy; our study is the first to relate both of these fluxes with the spatial pattern of a plant community.

We developed a spatially explicit model for predicting near-ground solar radiation and evaluated the relative roles of tree cover, height, and spatial pattern for sites along a grassland-forest continuum. We determined that a site's mean solar radiation depended on the amount of groundcover and on tree height but was independent of the spatial pattern of canopy patches, whereas its variance depended on all three. Lastly, we used our acquired knowledge and our developed models collectively to assess large-scale ecosystem responses to those climate variations that also lead to accelerated erosion.

Overall, this project demonstrated how spatial and temporal variations in fluxes of water and energy determine tight interrelationships between vegetation, soils, and climate in semiarid environments.

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Flare Star Monitoring with a New Single-Photon-Counting Imaging Detector

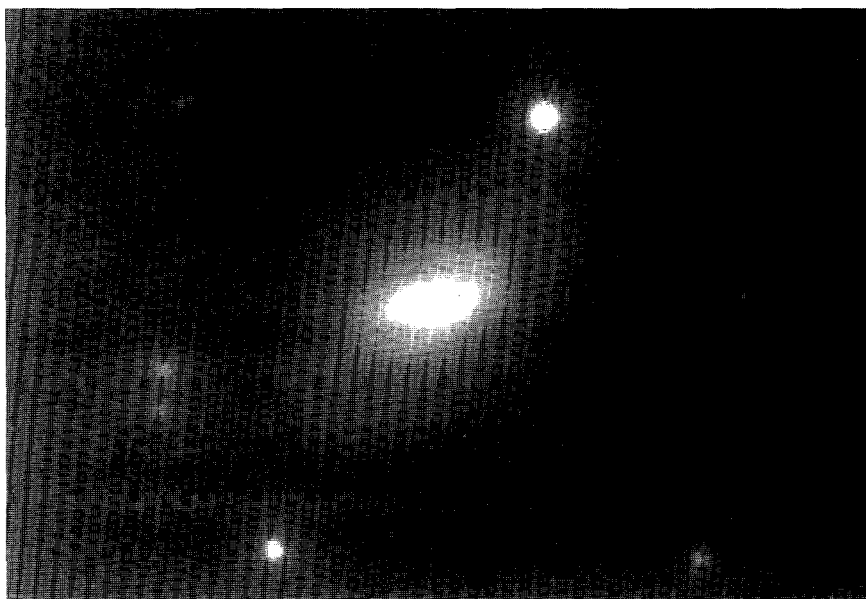
Donald E. Casperson

The objective of this project is to characterize optical transient phenomena in the nighttime sky, most notably flares from red dwarf stars, using a single-photon-counting imaging detector presently under development in another project. In addition to providing photon-counting sensitivity, this detector, a microchannel plate with crossed delay-line readout (MCP/CDL), provides high spatial as well as high temporal resolution.

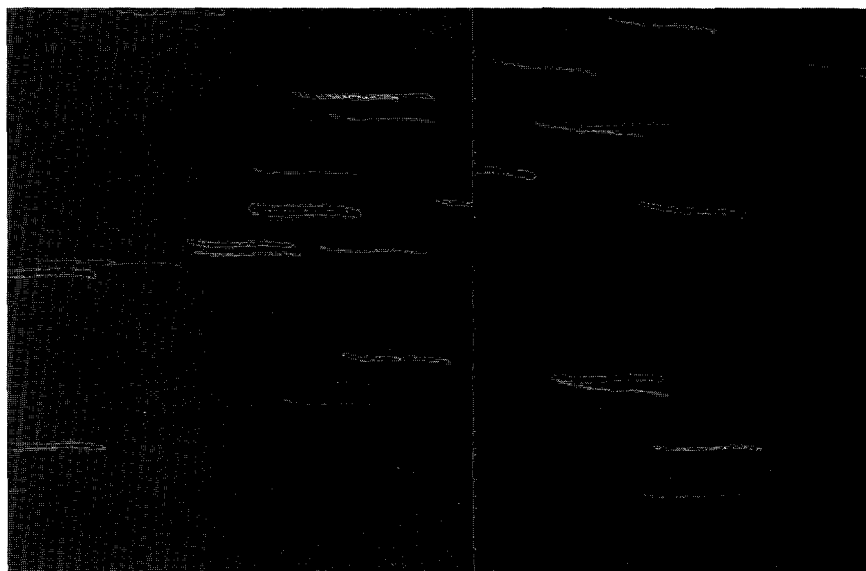
This year, we achieved major improvements in the detector readout, resulting in significantly higher photon-counting rates; however, successive photocathode and vacuum failures in the sealed MCP/CDL units have so far prevented the collection of any extensive data sets for our project. As a result, we have shifted our optical transient measurement work to two other directions.

First, we formed a collaboration with a NASA orbital debris tracking team that uses a charge-coupled device (CCD) camera at the 3-m-aperture Liquid Mirror Telescope (LMT) located in Cloudcroft, New Mexico. We have used a variant of this team's time-delay and integration (TDI) method for collecting stellar optical data with 1-s temporal resolution. The first accompanying figure shows an example of a barred spiral galaxy. The second figure shows stellar time-history tracks generated for this project. Both images were recorded with the CCD camera at the LMT.

In another effort related to all-sky monitoring of optical transients, we have contributed to the ongoing development of a remotely operable observatory that will be capable of recording visible images (in both TDI and standard framing format) with CCD cameras that are coupled to telescopes with programmable mounts.



Sample image of a barred spiral galaxy from the NASA 3-m-aperture LMT. This CCD camera image, courtesy of Mark Mulrooney (Lockheed-Martin/NASA/Johnson Space Center), was obtained with the TDI method and represents 96 s of total exposure. The V band stellar magnitude limit using this technique at the LMT is approximately $m = 22$.



Raw CCD image of stellar time-history tracks generated at the LMT using a variant of the TDI technique. For this image, the CCD sensor is rotated slightly relative to its position for the data of the previous figure. The 96-s integration of each stellar image is then uniformly distributed over a track of 100 CCD pixels, thus providing 1-s temporal resolution over each track. Lengthy TDI scans provide a very large database with which one can search for optical transients.

Close Encounters of Asteroids and Comets to Planets

Jack Hills

We are studying the physics of tidal encounters between comets, asteroids, and planets. In this study, we are making heavy use of an existing, robust few-body code to study encounters between the sun, planets, and asteroids (including double asteroids), and we are writing a code to study the breakup of an asteroid by the tidal field of a planet.

We believe that our work will explain a number of previously mysterious properties of asteroids whose orbits cross those of the inner planets. We will also determine the natural probability of capturing asteroids into orbits around Earth and the other inner planets by the tidal interplay between the sun and planets (and for Earth, that between the moon and Earth). In addition, we will determine the probability of asteroid capture—if the asteroid is double—by an exchange collision. We believe that this mechanism allowed Mars to capture its small moons. The permanent capture of asteroids around Earth would reduce the number of potentially dangerous collisions with Earth, and it may allow us to utilize the

resources of these captured asteroids for construction in space.

We have studied the tidal deformation of asteroids using an N-Body code. Most asteroids make several close approaches to Earth before they impact it. Many of the asteroids that intersect the orbit of Earth have extremely elongated shapes. We have found that the tidal field of Earth can produce elongations even larger than those yet observed if the asteroids have made close approaches to Earth. If their shapes result from tidal deformation, they are likely composed of loose blocks held together by gravity. This structure will have to be allowed for in any effort to mitigate their impact.

We have used an improved atmospheric model for asteroid collisions to study the capture of these objects into bound orbits around Earth as the result of grazing atmospheric collisions. The model uses a spherical atmosphere with a curve fit to the real atmospheric density rather than a plane-parallel atmosphere with exponential falloff in density. We have found that there is a narrow window

of atmospheric heights where an iron meteoroid would be captured into orbit by its energy dissipation in the atmosphere. However, stony meteoroids within a certain range of sizes can never be captured into bound orbit around Earth because they break apart easily in the atmosphere at the heights needed to cause enough energy dissipation to allow capture. Breakup greatly increases their dissipation cross section and causes them to plunge to Earth. We have also calculated the damage at ground level caused by such grazing colliders.

Publications

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Isotopic Prediction of Eruption Volume at Continental Volcanoes

Frank Perry

The goal of this project is to forecast eruption volume at stratovolcanoes using the neodymium isotopic composition of past eruptions. This model is based on the premise that the isotopic composition and volume of a magma are both controlled by influx of new magma into the system.

We obtained samples for two stratovolcanoes, Pico de Orizaba in southern Mexico and Daisen in southwest Japan. We selected these volcanoes because their eruptive history and eruption volumes are reasonably well documented. In order to assess the correlation between

eruption volume and isotopic composition, we chose the samples to represent a range of eruption volumes. Samples from both volcanoes were analyzed for neodymium, strontium, and lead isotopic compositions at University of California, Berkeley, and for major- and trace-element geochemistry at Los Alamos. Interpretation of these data may lead to a better understanding of what mechanisms control the magnitude of volcanic eruptions.

Experimental Cosmology: The Early Universe

Wojciech Zurek

We are using our N-body tree code on massively parallel supercomputers to test the standard cold dark matter (CDM) universe by conducting numerical studies of structure formation on the largest scales accessible to observations. These phenomena have recently become accessible to observations through both ground-based, very large telescope surveys and dedicated satellites.

Our simulations of the CDM model on parallel supercomputers (see the first two figures) have shown that the galaxy-galaxy velocity dispersion at small scales is consistent with results obtained from the sky survey done by the Harvard-Smithsonian Center for

Astrophysics. This finding is significant since velocity dispersion limits had been previously used to rule out the model. Similarly, we have shown that the redshift-space power spectrum (also used to rule out CDM) does not provide an unambiguous constraint at small scales and is consistent with the power spectrum measured in the Infrared Astronomical Satellite galaxy catalog. The comparison between the numerical experiments and the observations is not as straightforward as was usually assumed because of radial velocity skewness (a significant scatter of velocity dispersions between different observation-sized samples) and the importance of galaxy clusters.

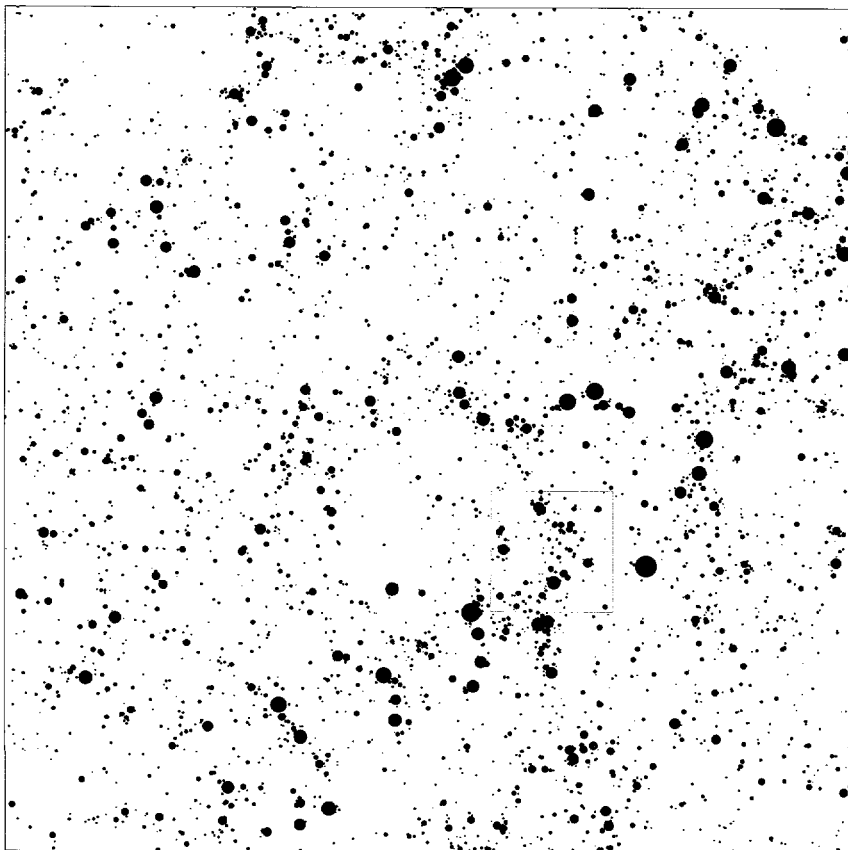
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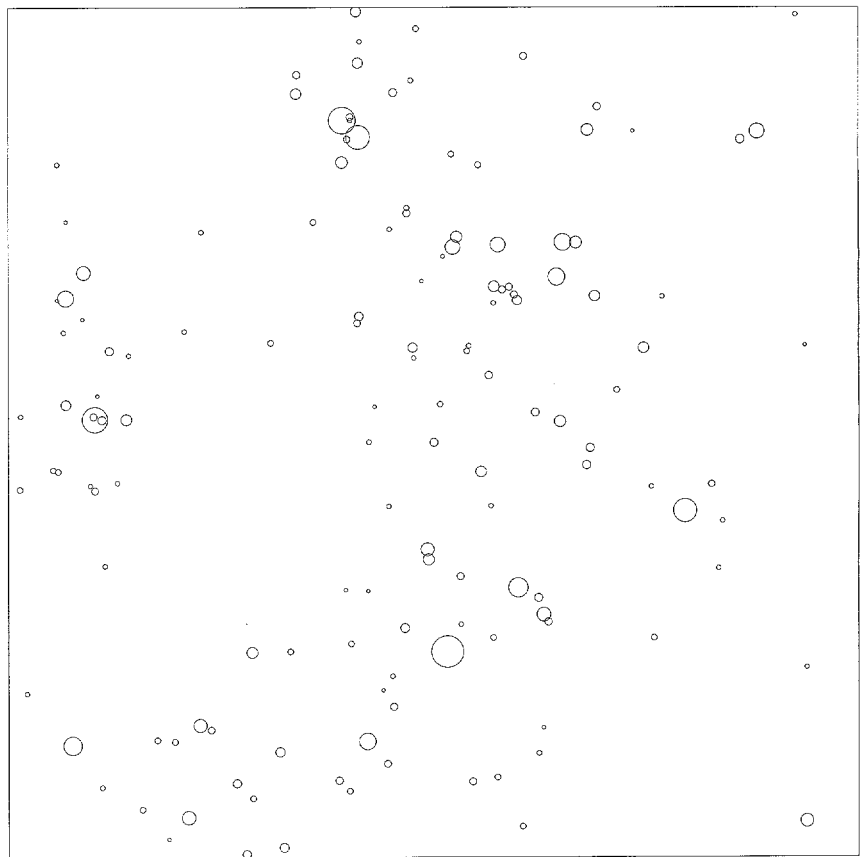
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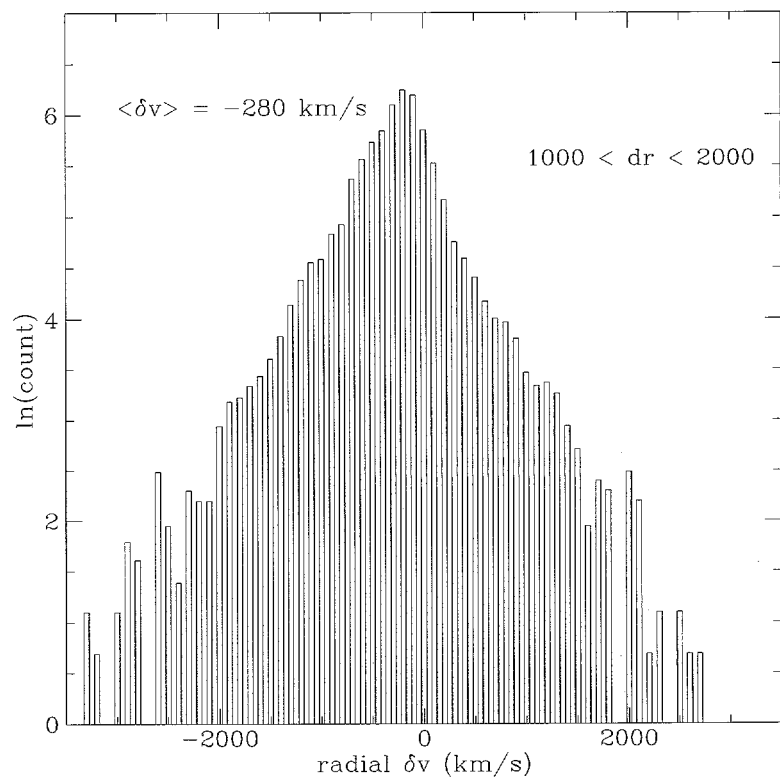


A plot of the projected locations of "galactic halos" in one of the N-body models. The size of the square is about 180 Mpc across. Sizes of the dots are approximately proportional to the masses of the halos. The small square indicates the region that is shown in more detail in the next figure.

A high-resolution plot of every particle (about 250,000 of them) in 1/50th of the total system (indicated by the small square in the previous figure), with the circles representing the location of galaxy halos.



Distribution of the number of pairs as a function of pairwise radial velocity. The triangular shape of this histogram over a large range of radial velocity difference (δv) implies that the distribution is indeed exponential, and the fact that the diagram appears isosceles allows us to infer the velocity dispersion (σ_v) from the slope.



Cosmology with Massive Neutrinos

Wojciech Zurek

The goal of this project is to understand the implications for cosmology of massive neutrinos and is motivated by the recent evidence for the neutrino mass obtained by the Liquid Scintillator Neutrino Detector experiment. We are conducting numerical studies of cosmological models with a significant mass fraction (20%–30%) attributable to light (several electron volt) neutrinos. We are focusing on two aspects of cosmic structure formation: (1) the present-day distribution and structure of galaxies and clusters; and (2) the number density of protogalactic objects at early times (redshift z of approximately 2).

In this research, an objective is to run fast, parallel-supercomputer simulations of massive-neutrino cosmologies with a resolution that is an order of magnitude better than has been previously attempted. The speed (more than 10 Gflops) and accuracy (~ 10 kpc spatial force resolution) of our code avoids problems of overmerging that have been reported by others, enabling us to understand the implications of massive neutrinos for cosmology, while setting cosmological constraints on neutrino mass.

The main accomplishment this first year is the development of a high-performance simulation code. Our parallel treecode now evolves cosmological density fields with periodic boundary conditions and hierarchical grids. Both are essential to accurately model large-scale neutrino free-streaming and formation of collapsed objects (galaxies and clusters) on small scales. In addition, we completed a battery of analysis codes, including redshift-space power-spectrum estimators and gravitational lensing/ray tracers.

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Global Climate Effects of the Emerging Chinese Transportation System

Scott Elliott

Nonpolluting bicycles have long been the predominant means of local surface transportation in the People's Republic of China. A major automobile manufacturing/importing effort has begun in the country, and planning documents indicate that the Chinese are making plans to acquire more than 100 million vehicles by early in the next century. We expect both regional- and global-scale pollution effects, judging from what the western world has experienced as a result of its large automotive fleets.

We are using the latest projections for the manufacture of Chinese automobiles to calculate potential pollution generation. For this investigation we are focusing on the oxidant, ozone. We have constructed emissions of the precursor species nitrogen oxides and volatile organics based on data for the eastern United States. We first estimated ozone production from values that we measured for continental/oceanic-scale yields relative to

precursor oxidation. We then corroborated the estimates through two-dimensional modeling of photochemistry in springtime airflow off the Asian land mass.

We expect the projected automobile fleet sizes to increase coastal and remote oceanic ozone by tens of parts per billion. We studied influences on the tropospheric aerosol system and on the major greenhouse gas, carbon dioxide, only peripherally. Nitrogen oxides created during the vehicular internal combustion process will contribute to nitrate pollution levels that will be measured in the Pacific. It is also likely that soot and fugitive dust will increase and that a significant rise in global carbon dioxide inputs will ensue.

Publications

Elliott, S., et al., "Atmospheric Effects of the Emerging Mainland Chinese Transportation System" (to be published in *J. Atmos. Chem.*).

Regge Geometrodynamics in Support of Gravity Wave Astronomy

Raymond Laflamme

The exciting feature of the emerging field of gravity wave astronomy is that these waves will allow us to probe deeper into cosmic events than we can by any other known means. While it is true that the parameterized post-Newtonian calculations have brought us far toward supporting such a probe, nevertheless, any integrated effect of cosmic coalescence will no doubt require the numerical solution of Einstein's equations.

We propose to solve Einstein's equations by employing the innovative and beautifully geometric approach known as Regge calculus (RC) in which the curved space-time

geometry is modeled by a lattice of four-dimensional triangles (simplices) in direct analogy with the two-dimensional triangulated nature of a geodesic dome. Recent developments in RC promise to make this truly independent tool numerically superior as compared with the finite-difference approaches. We are exploiting the unique geometric properties of RC and applying this numerical technique to the analysis of astrophysically relevant gravity wave generation and its subsequent detection by the Laser Interferometry Gravitational Observatory (LIGO).

We investigated the signature of the Lund-Regge metric on spaces of simplicial three-geometries, which are important in some formulations of quantum gravity. Tetrahedra can be joined together to make a three-dimensional, piecewise, linear manifold. A metric on this manifold is specified by assigning a flat metric to the interior of the tetrahedra and values to their squared edge-lengths. The subset of the space of squared edge-lengths obeying triangle and analogous inequalities is the simplicial configuration space. We have derived the Lund-Regge metric on this space and showed how it provides the shortest distance between simplicial three-geometries among all choices of gauge inside the simplices for defining this metric (Regge gauge freedom).

We showed analytically that there is always at least one timelike direction in simplicial configuration space and provided a lower bound on the number of spacelike directions. We propose to further evaluate the signature numerically for the simplicial configuration spaces based on some simple triangulations of the three-dimensional sphere (S^3) and torus (T^3). For the surface of a four-simplex triangulation of S^3 , we find one timelike direction and all the rest spacelike over all of the simplicial configuration space. For the triangulation of T^3 around flat space, we find degeneracies in the simplicial supermetric as well as a few gauge modes corresponding to a positive eigenvalue. We propose to extend this triangulation to a 600-cell model of a three-dimensional sphere. At each stage, we compared our results with the known properties of continuum superspace.

Publications

Hartle, J.B., W.A. Miller, and R.M. Williams, "Signature of the Simplicial Supermetric" (submitted to *Class. Quantum Grav.*).

Remote Sensing of Thundercloud Electric-Field Airglow

Joseph Borovsky

We predict that strong electric fields will enhance the cosmic-ray-produced background of airglow. The objectives of this project are to experimentally confirm the electric-field enhancement of the cosmic-ray-produced airglow near thunderclouds with photometers, measure the magnitude of the enhancement with photometers and compare the measurements with models, and spatially image the regions of enhanced airglow around thunderclouds. These images might allow a simple, reliable prediction of lightning.

In Fort Collins, Colorado, we made a ground-based campaign in the summer of 1996 and obtained images of sprites and sprite tendrils above thunderclouds and photometric data of the sprites. We used three intensified television cameras and one filtered photometer. Presently we are analyzing this data and preparing a manuscript.

Accretion onto Black Holes: The Power-Generating Mechanism

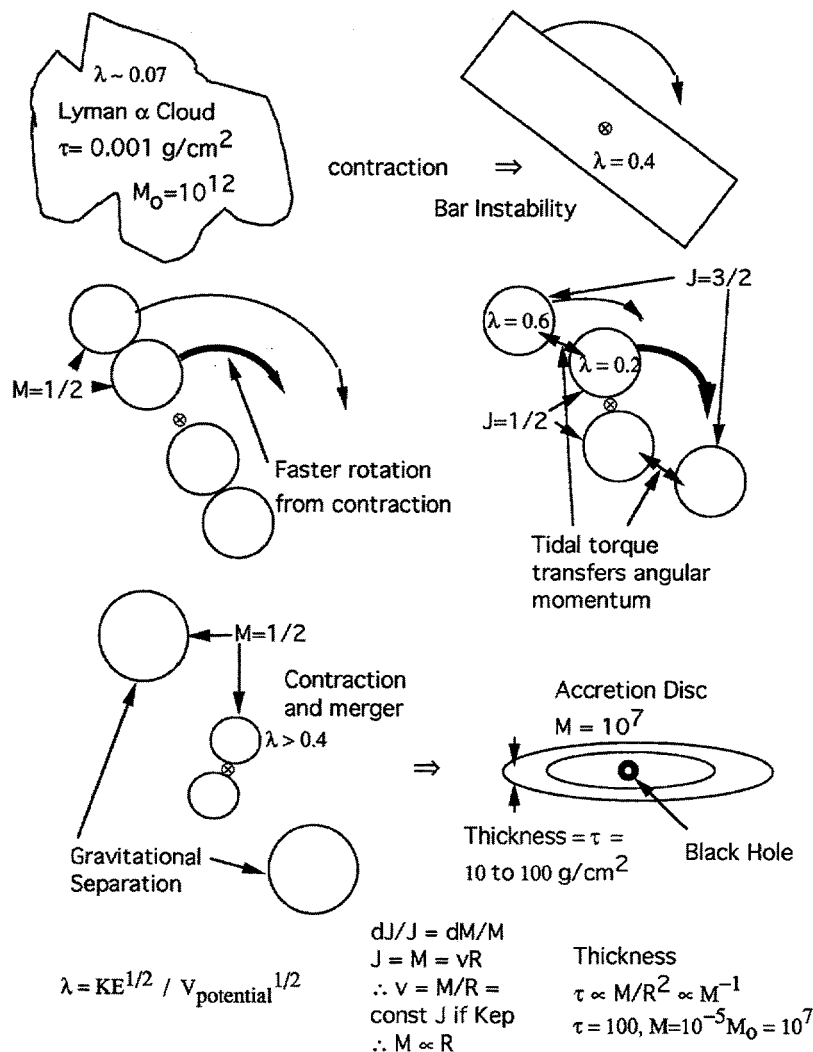
Warner Miller

Most objects in the observable universe have a reasonable explanation in terms of physics, although the details in depth may be missing or inconsistent. The outstanding few for which the basic concept is still elusive are gamma-ray bursts and the combination of quasars, so-called active galactic nuclei (AGN), and their associated collimated radio sources or jets. Our project is directed towards a consistent model of AGN and their jets. The most likely explanation of AGN is accretion onto a black hole from a Keplerian accretion disk, which is almost a unique explanation of the frequently observed, double-peaked, ultraviolet emission lines due to near-relativistic velocities in the disk.

We emphasized the physical relationships among the various phenomena: accretion disks, quasars, black holes, collimated radio sources, and galactic dynamos. Previously, these topics had been only weakly related without explicit cause and effect. We have constructed a model of the physical evolution from large, primordial density perturbations to "damped" Lyman-alpha clouds, to galaxy formation, to black holes, jets, and the galactic dynamo. We have derived the general relativistic distortions of radiation emitted from close to the black hole, thereby obtaining a new observational test of the central engine. See the accompanying two diagrams and the image for exemplary information about the AGN model.

The physics of accretion disks, the astrophysical dynamo, and magnetic reconnection are the least understood physical phenomena in astrophysics. They are still less understood in the general relativistic field close to the black hole. This lack of physical understanding frustrates a quantitative evaluation of observations that define

the evolution from the early universe to star formation. We have made progress in this understanding.



The collapse of a Lyman-alpha cloud of about $10^{12} M_\odot$ ($M_\odot$ = solar mass). The cloud is subject to barlike instabilities that form the bars during collapse and cause the bars to break up into smaller bars. The smaller bars collapse further and rotate faster. The mass of the arms of the smaller bars then torque the larger mass (m) at larger radii of the larger bars, and an exchange of angular momentum takes place. The angular momenta (J) scales such that $dJ/J = dm/m$. Then, the Keplerian velocity of the orbits of it is a constant. This constant velocity, independent of radius, is what is observed for almost all galaxies and leads to what is called a flat rotation curve and the prediction of dark matter. This scaling also leads to the mass ($10^8 M_\odot$) at which an accretion disk forms at the center of the galaxy; $M_\odot$ is what is needed to make the massive black hole.

Publications

Bromley, G.C., K. Chen, and W.A. Miller, "Line Emission from an Accretion Disk around a Rotating Black Hole: Toward a Measurement of Frame Dragging," *Astrophys. J.* **475**, 57 (1997).

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Stars that continuously collide (10^4 times) with the accretion disk (described in the previous figure) before disruption. These collisions explain the "broad emission lines" observed from quasars. Each collision makes a large plume of matter torn loose from the disk that will rise far above the disk. This plume will entrain any toroidal magnetic flux embedded in the disk. The expanding plume increases its moment of inertia and so will rotate more slowly than the rotating frame of the disk. This relative rotation of the plume and the disk twists any entrained magnetic flux, giving rise to the "alpha" effect in the alpha-omega dynamo. The omega deformation is the shear in the rotation rate of matter as a function of the radius of a Keplerian disk. This dynamo should make enough magnetic flux in the age of the disk, 10^8 years, to fill the galaxy with the observed galactic field of 3×10^{-6} G.

Disk Dynamo

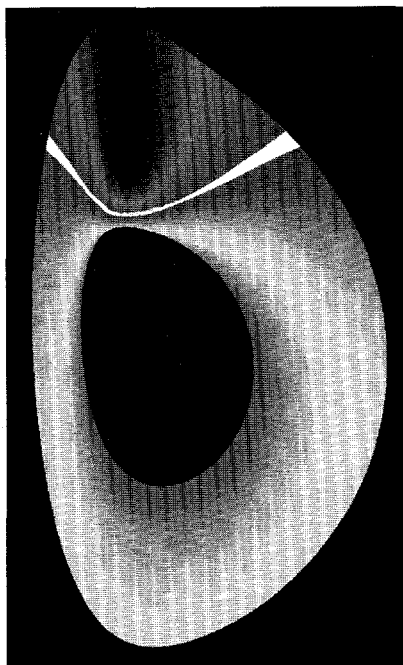
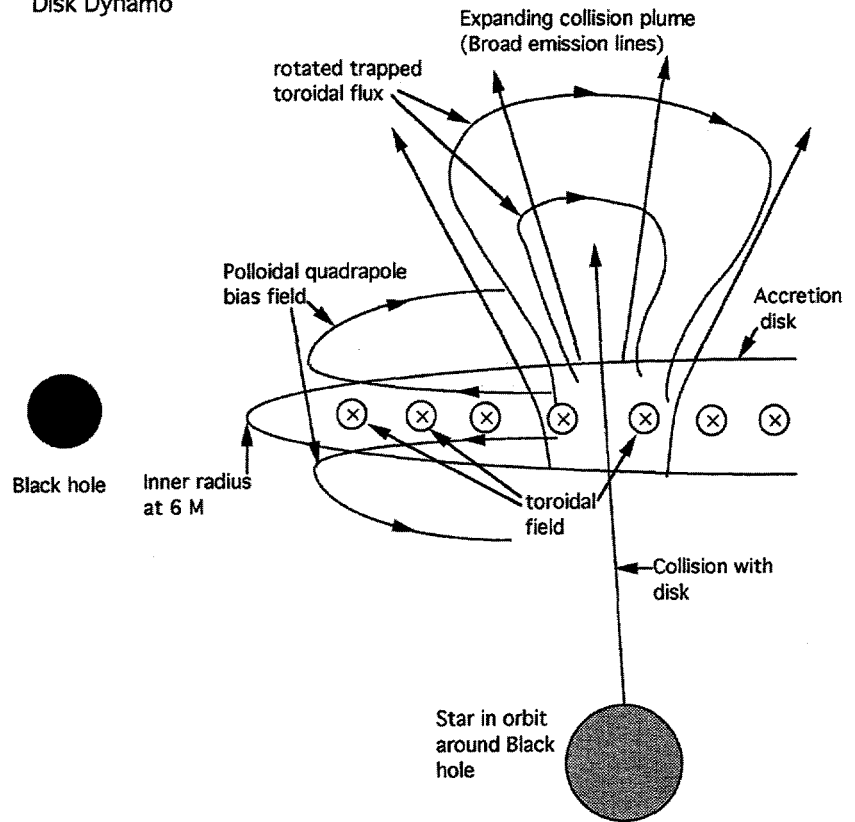


Image of a geometrically thin and optically thick accretion disk around a maximally rotating black hole of mass M . The inner radius and outer radius are at $1.25M$ and $10M$, respectively. This accretion disk is viewed at a 75° inclination. The false-gray-scale contour map indicates the ratio of observed frequency to emitted frequency; the dark, oval, shaded region at the top represents blue shift, and the bands around the radius indicate a red shift. The white (saturated) patch superimposed on the map contains the zero-frequency-shift contour.

Thermal Rocketing and the Laser Geodynamic Satellite (LAGEOS-1)

Warner Miller

LAGEOS-1 is the most accurately tracked satellite in orbit. It is a totally passive, dense, spherical satellite covered with 426 retroreflectors, which cause laser light to be reflected and returned along paths parallel to those of the corresponding incident rays. Besides its great utility in measuring the length of Earth's day and the polar wobble, this satellite can be used to measure, for the first time, the general, relativistic frame-dragging effect of Earth. This frame-dragging effect causes the inertial frames surrounding Earth to precess and is the gravitational analogue of a dipole magnetic field generated by a rotating current of charges.

Of the five dominant sources for error in measuring Earth's frame-dragging effect, the largest one involves interaction of the thermal forces on the surface of the satellite (or thermal rocketing) and the influence of such interaction on the nodal precession. The objective of our project is to enhance an already available code developed at Los Alamos to fit new optical-spin data recently obtained at the University of Maryland.

Enhancing our code involves three important tasks: (1) creating a more realistic model of Earth's magnetic field, (2) including the tidal precession on the line of nodes of the satellite, and (3) estimating the effect of the true geometry of LAGEOS-1

on our model predictions. The resulting code will then be used to model the new optical-spin data. By predicting how thermal forces will cause the satellite's orbit to change, the code will predict the future orientation of the satellite.

This year, we completed the first two major tasks, and we used the code to provide the first numerical model of the spin dynamics of LAGEOS-1. The results were consistent with the observations made at the University of Maryland. In particular, the drift of the spin axes of LAGEOS-1 toward the North Pole was correctly modeled for the first time. In addition, our code predicts a spin-orbit resonance phase that can dramatically affect the orientation of the satellite.

Our current code (including the enhancements completed this year) is more advanced than any other in the field. It will serve as the new spin-dynamics model for future LAGEOS satellite missions.

Plasmasphere Refilling: New Numerical and Observational Tools

Dan Winske

The outflow of plasma from the ionosphere and its interactions within the inner regions of the magnetosphere remain important problems in space physics. While outflow is a continuous process, it becomes even more important after geomagnetic substorms, when magnetic field lines that have been vented of plasma are reconnected and the empty flux tubes are refilled with outflowing plasma. The purpose of this project is to develop new computational, theoretical, and observational tools to study the dynamics and heating associated with the plasma outflow and refilling processes.

We developed new numerical tools to model the transition from collisional plasma flow at low altitudes (~200 km) to collisionless behavior at high altitudes (~4000 km) and

incorporated these tools in a multispecies kinetic model of the outflow process. We also investigated electromagnetic instabilities in the outer magnetosphere to understand their contribution to the heating of upflowing protons and minority ions (such as helium). In addition, we have used new observational techniques to analyze low-energy plasma data from satellites in geosynchronous orbit and to assess the effect of a spacecraft's electric potential (typically a few volts) on these data.

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Nuclear and Particle Physics

Time-Reversal Tests in Polarized Neutron Reactions

J. David Bowman

The goal of this project is to develop cells of polarized ^3He to use as polarizers and analyzers of neutron spin. The interaction of polarized ^3He with neutrons is highly spin dependent. Neutrons that have their spin parallel to the ^3He polarization are absorbed. The ^3He nuclei are polarized when cells containing rubidium vapor are illuminated with circularly polarized light from diode lasers. The valence electron in the rubidium atom absorbs the laser light and becomes polarized. The atomic polarization is transferred to the ^3He nuclei by

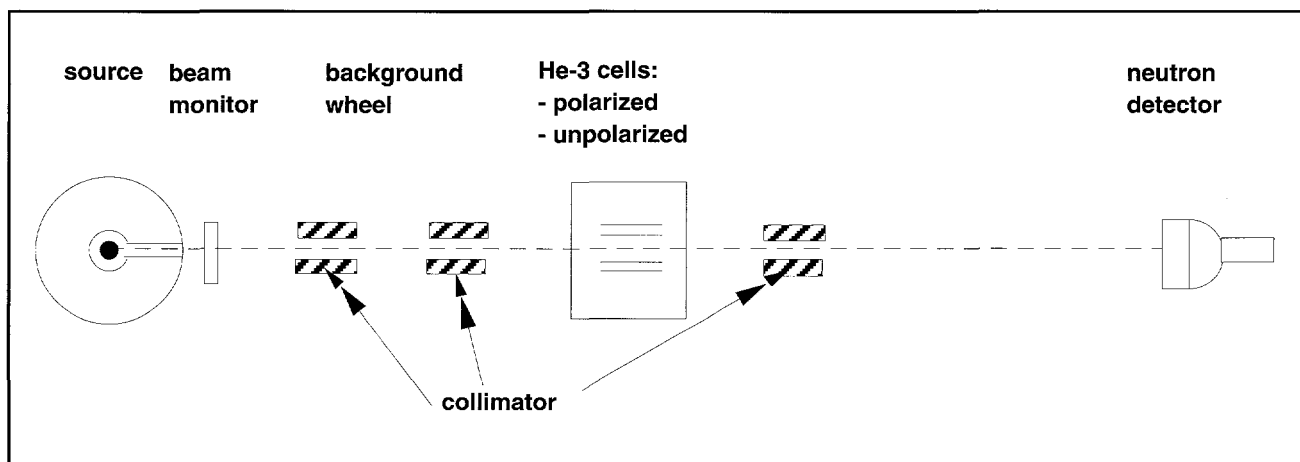
collisions. In order to use these polarizers and analyzers in tests of time reversal, it is necessary to construct cells, polarize the ^3He , and measure the polarization of the neutrons after passage through the cells.

We have built the apparatus needed to produce cells of polarized ^3He . This apparatus incorporates diode lasers, optics, Helmholtz coils, nuclear magnetic resonance pickup coils, and lock-in amplifiers. We are developing cells in which the natural boron in the glass is replaced by isotopically

separated ^{11}B . These cells are needed for work with cold neutrons because the absorption cross section of natural boron for low-energy neutrons is large. We have measured the polarization of neutron beams polarized by ^3He with an accuracy of 1% by using the parametric relationship between the transmission of neutrons through the cells and their polarization. We have developed the apparatus and techniques needed to improve the accuracy to 0.1%. The accompanying figure shows the measurement apparatus.

Publications

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Apparatus to measure precisely the polarization of a neutron beam prepared by a ^3He polarizer. The Manuel Lujan Jr. Neutron Scattering Center neutron source produces a short, intense pulse of neutrons having a broad range of energies. The neutron energy is precisely measured by observations of the time it takes each neutron to reach the detector, located 56 m from the source. The polarized ^3He cell and a dummy cell are alternately placed in the beam. The ratio of transmissions, $R(0)$, is measured with the ^3He cell unpolarized. The ^3He cell is polarized, and the ratio $R(p)$ is measured. The polarization of the neutron beam, P , is then obtained as $P = [1 + (R(0)/R(p))^2]^{1/2}$.

Exploring and Testing the Standard Model and Beyond

Geoffrey West

In this project we are primarily working to understand, and ultimately to explore, the limitations of the universally accepted Standard Model of elementary particles, which incorporates their strong and electroweak interactions. As an outgrowth of that, we are investigating possibilities for unifying all of the fundamental forces of nature, including gravity. We anticipate that such frontier research will have phenomenological implications for prospective programs and experiments.

Last year we worked on the unification of the concepts of scaling and fractals with the renormalization group. This year we extended our work to give a fractal description of the nucleon in a generalized quantum chromodynamics (QCD) parton model to biophysical systems such as the cardiovascular and respiratory systems.

We showed how duality in supersymmetric QCD follows from nonperturbative instanton configurations. We estimated the masses of light quarks using lattice QCD—our estimates are considerably smaller than the values commonly used and have important implications for the charge-parity-violating parameters. Also this year, we continued to explore the interface of quantum and classical chaos based on our discovery of semiquantum chaos, and we continued work on the conformal anomaly, proving the effects of the theory. We wrote several major reviews, some in response to solicitations. We were also invited to give talks on our work at many major institutions worldwide as well as at international conferences and workshops.

Publications

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Dorey, N., V.V. Khoze, and M.P. Mattis, "Multiinstanton Check of the Relation between the Prepotential-F and the Modulus-U in N=2 Susy Yang-Mills Theory," *Phys. Lett. B* **390**, 205 (1997).

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Habib, S., E. Mottola, and P. Tinyakov, "Winding Transitions at Finite Energy and Temperature: An O(3) Model," *Phys. Rev. D* **54** (12), 7774 (1996).

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L3 Physics at the Z Resonance and a Search for the Higgs Particle

W. Kinnison

This project is a study of the Standard Model of electroweak interactions using the L3 detector of the Large Electron-Positron Collider (LEP) at the European Center for Nuclear Science. During the reporting period, we developed a new method of vertex finding that is applicable for most colliding-beam, high-energy physics experiments, and we used the methodology to analyze L3 data for a published paper on R_b , which is a measure of the amount of b-quark production in hadronic decays of the Z^0 .

To carry out the analysis, we invested a considerable amount of effort in improving the alignment

information and analysis techniques for several components of the L3 detector including the "z chambers," which had never before been used successfully to analyze L3 data. Additionally, we used the silicon microvertex detector—which Los Alamos had a major role in proposing, designing, building, and commissioning—for its first time in making a complete physics analysis. Both the improvements in the overall analysis of L3 data and the specific new vertex-finding algorithms that we developed are now being used by the entire L3 collaboration in many new physics analysis projects, including b-meson tagging, which is required for the Higgs meson search at LEP.

Neutrinos and Theory of Weak Interactions

Joseph Carlson

We are studying low-energy measurements of parity violation in nuclear systems, astrophysical reactions involved in solar neutrino production, neutrino interactions, and time-reversal violation in extensions to the Standard Model.

Parity Violation in Few-Body Systems. We are analyzing the prospects for measuring the parity-nonconserving asymmetry A in polarized neutron-plus-proton radiative capture at the Los Alamos Neutron Science Center (LANSCE). The goal of the experiment is to extract a definitive value for the weak pion-nucleon coupling constant. Experimental work to date has produced only upper limits to this coupling.

We have calculated the parity-conserving contributions to A , which had been tacitly assumed to be negligible. We have shown that experimental "tricks" are required to suppress this contribution to A below the 10^{-8} level sought in our experiments. We have also performed a microscopic analysis of parity violation in the transmission of polarized ultracold neutrons through helium. At these energies, the parity-violating neutron-neutron interaction results in a spin rotation in the polarized neutrons. We performed microscopic five-body calculations of neutron-alpha scattering using realistic two- and three-nucleon interactions. We continue to find that the pion-exchange term is dominant, but with the opposite sign to that predicted in simple models.

Time-Reversal Violation. The most economical explanation of charge-conjugation parity (CP) violation in the Standard Model is given by the phase δ of the Kobayashi-Maskawa model. One can search for additional CP-violating interactions in

extensions of the Standard Model by determining observables where the effects of δ are suppressed. In the Kobayashi-Maskawa model, CP-violating effects in beta decay (and in other semileptonic processes) arise also only in second order in the weak interaction.

We have calculated the contribution of δ to the T-odd D- and R-correlations in beta decay. These correlations are time-reversal-odd scalar products of the momentum of the electron and neutrino and the nuclear spin. We find $D = 10^{-12}$ and $R = 10^{-14}$, compared with the best present experimental limit of 10^{-3} . We have calculated D and R also for the theta-term in the quantum chromodynamics Lagrangian, a second source of CP violation in the Standard Model. With the present experimental limit for theta, we obtain $D = 10^{-14}$ and $R = 10^{-12}$. The small values of D and R in the Standard Model leave a large window in which to search for new types of CP-violating interactions. We have also investigated scalar-type, CP-violating, muon-quark charged-current interactions in extensions of the Standard Model. These interactions contribute to T-odd observables in muon capture, which provide information complementary to that provided by nuclear beta decay.

Neutrino Properties and Interactions. We extended our theory of an additional scalar interaction to forms involving three neutrinos. The additional coupling introduced does not alter the successful phenomenology of the Standard Model. We find that there is a repulsive effect from the scalar field of a large vacuum-mass neutrino on the local density of a light vacuum-mass neutrino. The result is that the neutrino clouds we found previously may have a complex internal structure, such as consisting of spherical annuli (with gaps)

surrounding a central cloud. Because the effective masses of the neutrinos may become equal and opposite in the regions in which the scalar field strength is rapidly varying, enhancement of neutrino-mixing oscillations may occur in such regions.

Publications

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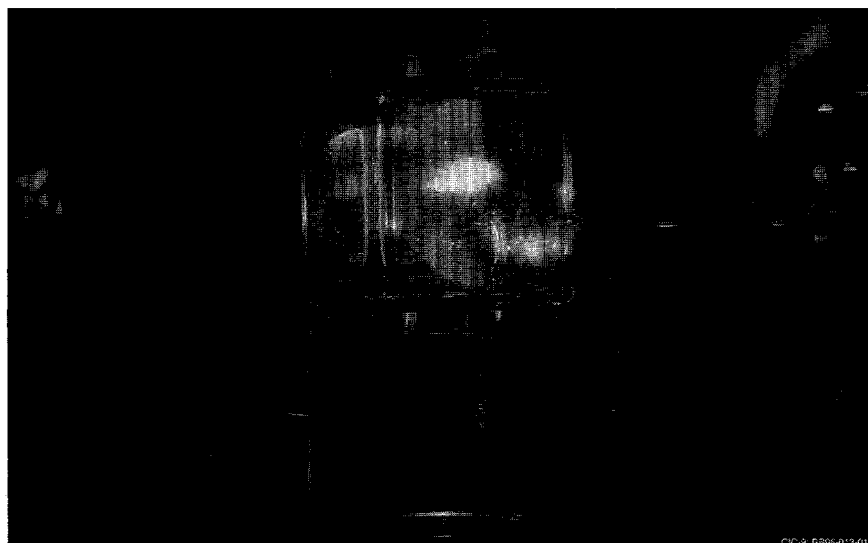
Weak Interaction Measurements with Optically Trapped Radioactive Atoms

David Vieira

The main objective of our project is to develop the technology that will ultimately allow a high-precision test of electroweak interactions in atomic nuclei. To achieve this, we are focusing our efforts on the beta-asymmetry measurements of polarized ^{82}Rb ($t_{1/2} = 75$ s). The key technology needed to undertake this work is the efficient optical and magnetic trapping of radioactive

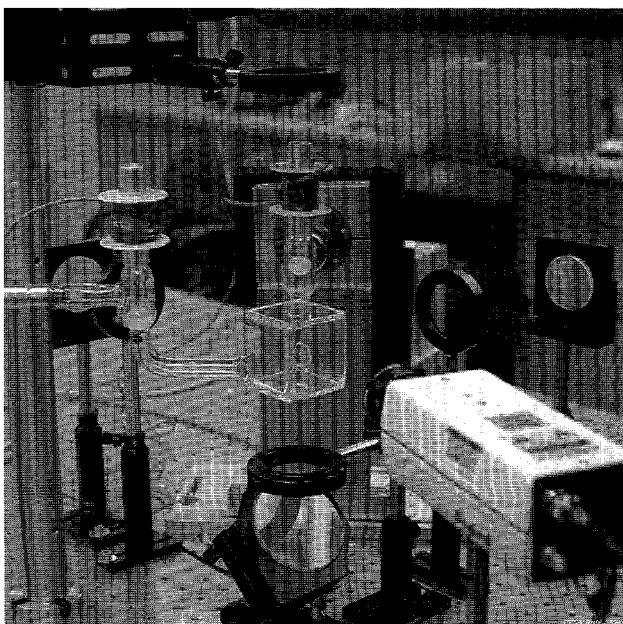
atoms. A magneto-optical trap (MOT) consists of six circularly polarized, counterpropagating laser beams, which, in combination with a pair of anti-Helmholtz coils, enable the cooling and trapping of atoms. A high-intensity MOT can easily trap 10^{10} atoms out of the vapor state (see the first figure); however, the trapping of radioactive atoms requires that the trapping process also be efficient.

We have taken two steps to ensure high trapping efficiency. The first step is to use a special nonstick octadecyltrichlorosilane (OTS) dry-film coating on the glass trapping cell to prevent the "sticking" of alkali species to the walls. Using the OTS-coated glass cell shown in the second figure, we have measured a trapping efficiency of 20% (see the third figure). This efficiency exceeds currently published trapping efficiencies by a factor of 3 and reflects the improved trapping geometry of our MOT. The second step involves gas-free sample loading using a mass-separator ion implantation and release method. To this end, we have recently coupled a MOT to an existing, and now upgraded, mass separator. We



An infrared picture of a fluorescing cloud of $\sim 10^{10}$ cesium atoms trapped in a high-intensity, magneto-optical trap. The pancake-shaped cloud is approximately 15 mm in diam $\times$ 10 mm thick.

A picture of a dry-film-coated glass cell (50-mm cube) with two remotely controlled glass valves used in the MOT measurements of trapping efficiency. The valve on the left is connected to a cesium reservoir, and the valve in the background is connected to a 20-L/s ion pump.

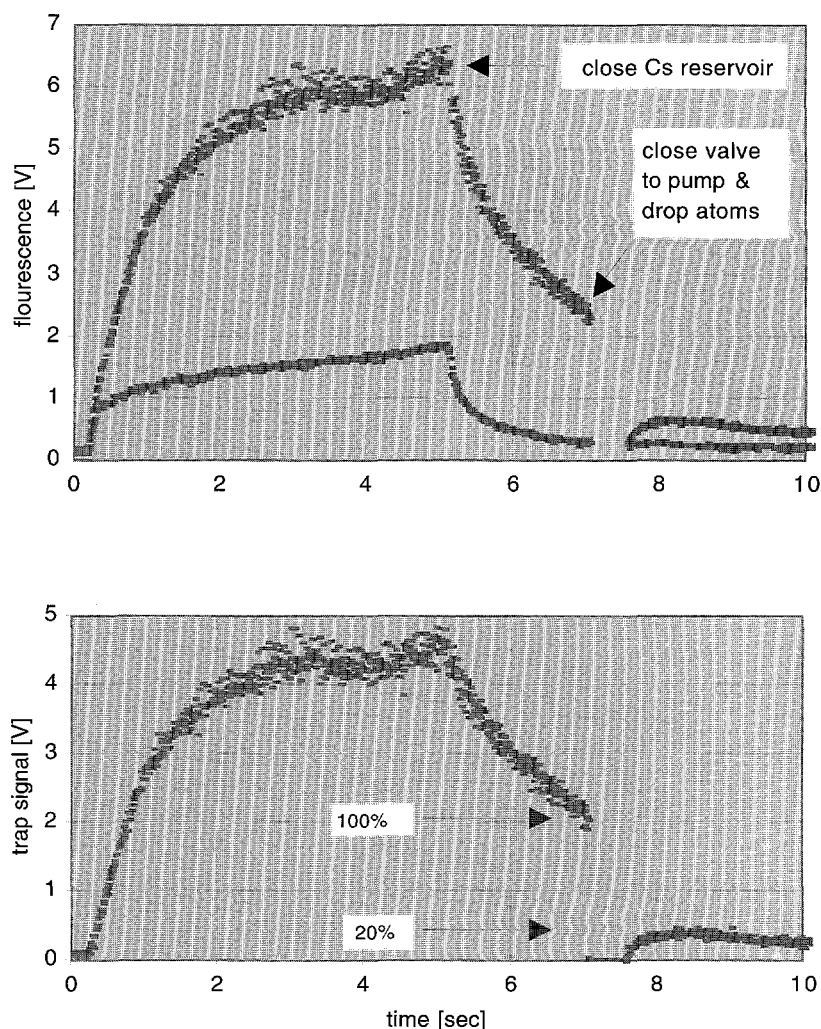


have made good progress in implanting and releasing stable rubidium species, and the high-efficiency trapping of ^{82}Rb is near at hand.

Publications

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Guckert, R., E.P. Chamberlin, D.W. Preston, et al., "Coupling an Optical Trap to a Mass Separator" (to be published in *Nucl. Instrum. Meth. Phys. Res. B*).



Results of fluorescence-derived efficiency measurements. The upper trace in the upper figure shows the trap filling as the valves to the cesium reservoir and ion pump are both open. At 5 s, the valve to the cesium reservoir is closed, and the fluorescence signal drops as atoms are slowly lost from the trap and untrapped cesium atoms are pumped out. At 7 s, the fluorescence signal is dominated by the number of trapped atoms, and the height of this signal measures their number. The trap is then turned off by shuttering the trapping laser light and turning off the magnetic field. At 7.5 s, the trap is turned back on and it refills. The relative height of the fluorescence signals measures the trapping efficiency. The bottom trace in the upper figure measures the background fluorescence signal obtained when the magnetic field is reversed in the nontrapping direction. The bottom figure shows the differences between the two traces given in the upper figure. A 20% retrapping efficiency is determined.

Neutrino Physics at Fermilab

Fred Federspiel

The Los Alamos liquid scintillator neutrino detector (LSND) has recently reported strong evidence for neutrino oscillations (and, hence, neutrino mass). If verified, this result will have profound consequences for nuclear and particle physics, cosmology, and astrophysics. We plan to carry out an experiment at Fermilab to verify the LSND result and accurately determine the parameters of the oscillations.

There has been considerable recent progress in the development of high-speed, charge-coupled detector arrays

at Los Alamos. We are investigating the application of this new technology to particle physics detectors. This promising new idea could potentially revolutionize the field of neutrino physics by enabling the construction of massive, highly segmented detectors at a cost of ~100 times less than a similar-sized, conventionally instrumented detector.

Our progress to date has been in three areas: (1) design of a neutrino production facility; (2) calculation of

expected signal and background rates; and (3) design and simulation of a detector. Our baseline design for the neutrino production facility has met its design goal of providing a pure muon-neutrino beam with contamination less than 0.5% electron neutrinos. The calculation of background rates has allowed us to establish the following particle identification requirements for the detectors: fewer than 0.1% of muons along with fewer than 1% of pions may survive electron selection criteria. Now that we have established these design goals for the detector, we are pursuing the development of capable detector technologies.

A Continuous Watch of the Northern Sky above 40 TeV with the CYGNUS Array

Cyrus Hoffman

We have been using the CYGNUS air-shower array to search for episodes of ultra-high-energy (UHE, >40 TeV) gamma-ray emission from astrophysical objects. Given that such emissions are only sporadic, it is important to keep a continuous watch on the sky. The array operated well during most of FY 1996 to allow our research, but in August 1996 a fatal hardware error occurred in the CYGNUS data-acquisition computer, shutting down the experiment.

We could not continue the CYGNUS experiment after the repair because a more powerful detector, Milagrito (a prototype for the Milagro detector), had been installed. Milagrito will be available for data taking later in the fall of 1996. Because of its lower energy threshold (~500 GeV), this new detector is much more sensitive than CYGNUS to gamma-ray emission from astrophysical objects; our sky watch experiment for UHE gamma-ray

bursts will continue when Milagrito comes on-line. At this time, the analysis of the CYGNUS data shows no evidence of UHE emission from any source.

We have also used the pools at CYGNUS to experimentally test the concept of searching for gamma-ray emissions from gamma-ray bursts by monitoring the single rates of individual photomultiplier tubes in a water Cerenkov counter. The results of these tests are encouraging. If successful, this method should be applicable to both Milagrito and Milagro and should enhance the sensitivity of these detectors to emissions from gamma-ray bursts.

Neutron Measurements to Optimize Treatment of Cancer Patients with Fast Neutrons

John Ullmann and Robert Haight

Data for the interaction of neutrons with biological elements are important for radiation therapy and radiation protection dosimetry. Data for carbon, and especially oxygen, are greatly needed. We have set up a system for detecting charged particles

produced by neutron interactions in the energy range up to 150 MeV. A new beam line and new electronics have been developed at the Weapons Neutron Research facility of the Los Alamos Neutron Science Center (LANSCE). We are beginning to

characterize the experimental apparatus and approach and to take preliminary data. This capability will put us in a good position for proposing a larger experimental program in FY 1998. Some interest has been shown in our capabilities by the Accelerator Production of Tritium program.

Publications

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Antiquark Distributions in the Proton

Jen-Chieh Peng

The study of quark and antiquark distributions in the nucleon has been a major endeavor in nuclear and particle physics. Results from a recent deep-inelastic scattering experiment suggest the surprising possibility that the up-and-down antiquark distributions in the proton are not symmetric. We can directly determine the antiquark distributions in the proton by comparing the Drell-Yan cross sections on hydrogen versus deuterium targets. A new experiment (E866) is in progress at Fermilab to carry out such measurements.

We are performing E866 with an 800-GeV proton beam, together with

a high-resolution, high-rate magnetic spectrometer. Other experiments do not match the expected statistical accuracy and range of coverage in x (fraction of nucleon momentum carried by the antiquark). E866 will have sufficient accuracy to test all theoretical models that predict asymmetric up-and-down antiquark distributions. We will also obtain additional data on the production of J/ψ and ψ resonances (bound states of heavy quarks) in E866.

The E866 has been taking data since September 1996. Preliminary results show that the apparatus is working very well. We anticipate

having at least six months of beam, which will allow us to achieve the sensitivities for a definitive measurement of flavor symmetry of sea quarks in the proton.

Publications

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Nucleon-Nucleon Data Analysis

Michael W. McNaughton

The objective of this project was to analyze and publish two sets of nucleon-nucleon (NN) data. These are the final sets of data to complete the set of NN measurements at the Los Alamos Meson Physics Facility (LAMPF) and determine the NN-scattering amplitudes from 485 to 800 MeV.

These new data are the most accurate in the world, with precision better than 1% and absolute accuracy about 1%. With the inclusion of these data, all known ambiguities in the phase-shift analysis are resolved, and the final phase-shift solutions are unique.

The measurements of the proton-proton (pp) elastic cross section are in excellent agreement with previous results from LAMPF. These data have stabilized the NN phase-shift analysis and determine the absolute normalization of both nucleon-nucleon and

nucleon nucleus data obtained at LAMPF over the past 20 years.

The analyzing power data resolve the ambiguity in the absolute normalization of the LAMPF polarized neutron beams. In addition, they strengthen the conclusion that isospin-zero inelastic scattering is strongly coupled to a pair of delta resonances, and is therefore very small at 800 MeV, since 800 MeV is far below the mean energy of 1380 MeV required to create two deltas.

Publications

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Solar Neutrino Physics

Andrew Hime

Our project focuses on extracting the neutral-current signal from the Sudbury Neutrino Observatory (SNO) using an array of ultralow-background ^3He proportional counters. In the past year, the neutral-current detector (NCD) project moved from the R&D phase toward full-scale construction. Los Alamos has played the lead role in defining the operating parameters and constraints for the NCDs, including requirements for gas fill and purification and for optimizing the detectors to collect the most significant data.

Much of our effort has focused on designing and constructing a large gas-handling system, which has been combined with our main "NCD factory." While the optimization of operating parameters is now essentially complete, in the coming year we will continue our detector test-bench studies to refine the front-end electronics. This part of the project is related to our more general goal of developing data reduction and analysis tools for detecting neutral-current signals.

Monitoring and controlling backgrounds are still significant aspects of the NCD program. Our radioassays played an important role during the design phase and will be used continuously during the production phase to monitor detector components. Information on the radiopurity of detector construction materials is essential for extracting the neutral-current signal from SNO in the presence of photodisintegration backgrounds.

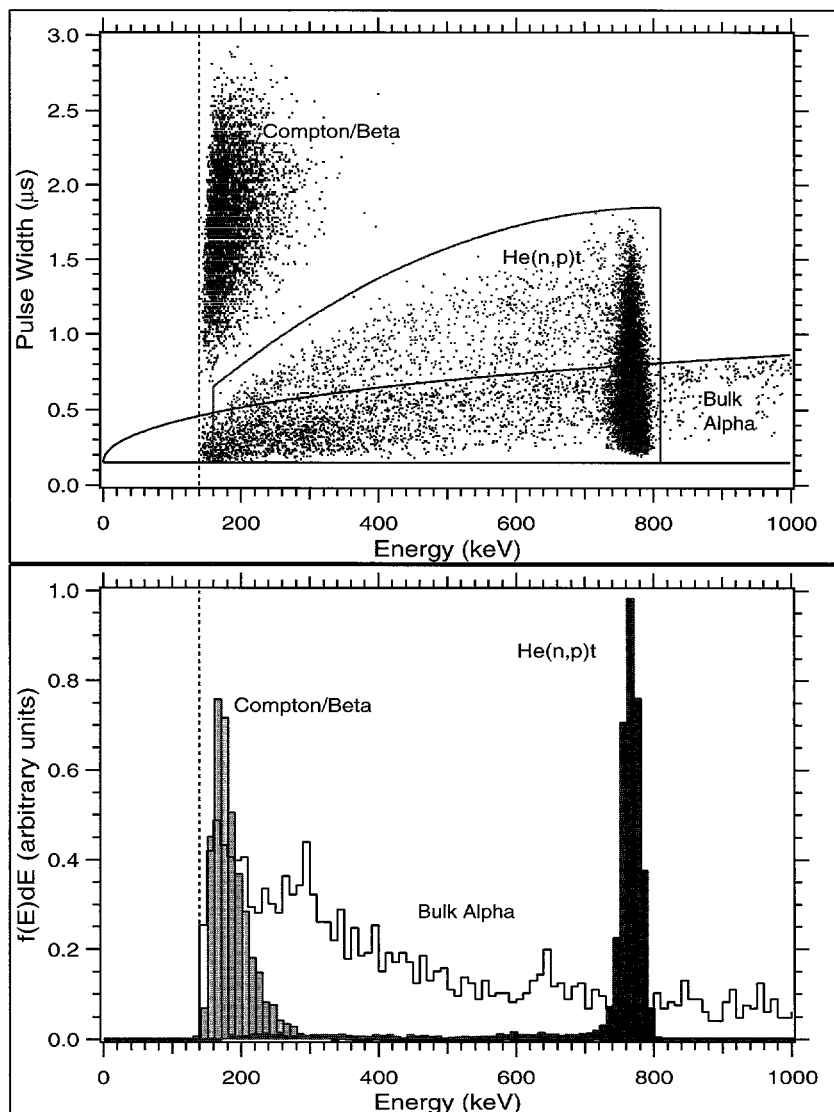
We are continuing to study detectors at our low-background counting facility at the Waste Isolation Pilot Plant (WIPP). This work will help us establish acceptable intrinsic backgrounds and contribute to the development of our signal extraction and pulse-shape discrimination techniques (see accompanying figure). Data from our low-background experiments is

used in parallel with our detector test-bench studies to optimize our use of digitized waveforms to extract signals and identify events. We are currently using the information contained in the digitized waveforms to extract in real time the photodisintegration background signals from the alpha distributions registered in the NCDs. In the upcoming year, we will extend these activities to include more

sophisticated methods, such as event-by-event pulse-shape fitters, maximum entropy techniques, and neural networks, which promise to maximize our ability to discriminate neutral-current events from background signals.

Publications

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Scatter plot demonstrating our pulse-shape discrimination capabilities using event topology from $\text{He}(n,p)t$ events, bulk alpha activity, and gamma-induced Compton electrons.

Chiral Symmetry in Finite Nuclei

David Madland

The goal of our project is to understand chiral symmetry in finite nuclei. As a first step, we have published the physical reasoning and principal evidence demonstrating the role of chiral symmetry in finite nuclei. To be able to continue this work, we have made the necessary changes and additions to our two main computer codes. We have modified the generalized, nonlinear, least-squares, adjustment algorithm LACHI that determines the coupling constants of the chiral Lagrangians. We have modified the algorithm by (1) introducing the covariance matrix in order to study the correlations among the various coupling constants; (2) redefining the chiral Lagrangians so that their coupling constants form a

search vector whose elements are of order unity if naturalness holds; and (3) deleting proton states that are only quasibound inside the Coulomb barrier. Given a set of coupling constants, the predictive algorithm LANUC solving the Dirac-Hartree equations self-consistently for each test nucleus has been made compatible with (2) and has the change specified in (3).

We have also determined the main elements (existing FORTRAN routines) that will be used to construct a new, nonlinear, least-squares, adjustment algorithm that will be mounted on an Ultra-SPARC workstation. Finally, with the improved codes, we have found a new minimum chi-square for which seven of the nine

coupling constants are natural, as opposed to only six in our initial work. In fact, the new value of chi-square is also lower, but the predictive power is somewhat worse.

Publications

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Simulating the Decays of Bottom and Charm Mesons

Tanmoy Bhattacharya

Our objective is to carry out a detailed study of the decay properties of bottom and charm mesons by simulating the Standard Model of strong interactions on the lattice. We believe that the capabilities of the massively parallel machine, CM5, at the Advanced Computing Laboratory (ACL) will allow us to produce definitive predictions in this field, and put the standard model to stringent tests in present and proposed experiments. In addition, we shall work in close collaboration with the staff scientists at the ACL to help develop hardware and software optimization tools and graphics, which will contribute significantly to the Laboratory's growth as a forerunner in advanced computing.

During the reporting period, we developed the code required to simulate the bottom quark on a lattice with a view to carrying out a detailed study of the decay properties of the bottom and charm mesons. The code was developed in close collaboration with the ACL on the CM5 there. The code uses the nonrelativistic formulation of quantum chromodynamics to simulate the heavy quarks and the $O(a)$ improved light fermions on a $16 \times 16 \times 16 \times 48$ lattice. The physics analysis is done combining these two types of quarks together to study the properties of hadrons made up of heavy-heavy, heavy-light, and light-light quarks. We have so far analyzed 75 lattices and have preliminary

results (based on this data set for the mass spectrum and decay constants of heavy-light mesons). We are now in the process of adding in the physics analysis for the study of semileptonic form factors and matrix elements of 4-fermion operators and increasing the statistical sample size.

Publications

Ali Khan, A., and T. Bhattacharya, "B and Bc Mesons with NRQCD and Clover Actions" (to be published in *International Symp. on Lattice Field Theory Proc.*).

Nonequilibrium Dynamics of the Quark-Gluon Plasma in Heavy-Ion Collisions

Emil Mottola

We have developed field theory and numerical methods for the general problem of quantum back reaction on classical fields, with applications to a wide variety of physical systems. Our main focus was on particle production processes in the time evolution of the quark-gluon plasma following an ultra-relativistic heavy-ion collision. In particular, we studied in some detail the evolution of a disoriented chiral condensate (DCC) produced in the chiral phase transition of nuclear matter in heavy-ion collision experiments, as shown in both accompanying figures.

We have also studied dissipation and decoherence due to particle production in time-varying mean fields. We modified numerical codes previously developed for particle production in strong electric fields in quantum electrodynamics for the quantum chromodynamics problem. We have made specific predictions for energy-momentum flow and pion production in the central rapidity region of experiments to be performed at the Relativistic High-Intensity Collider.

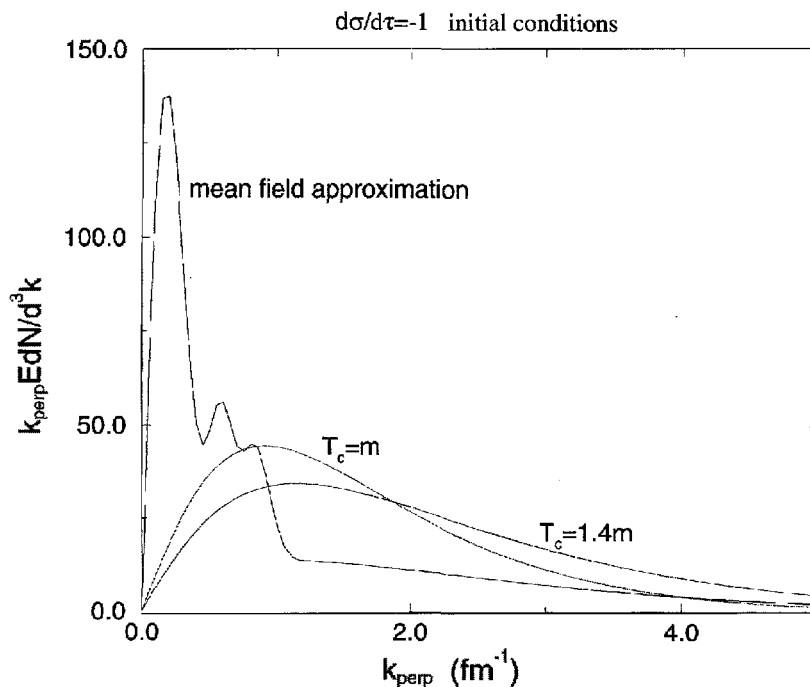
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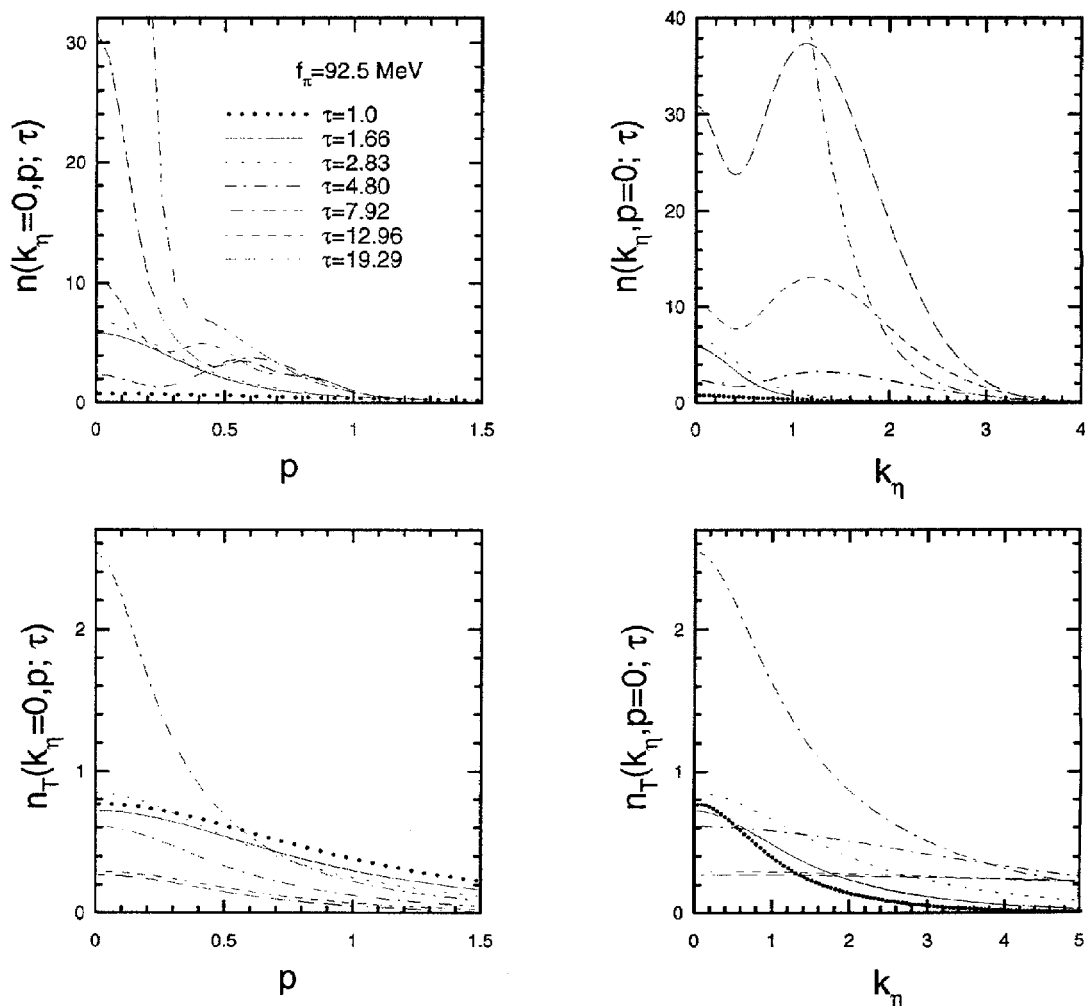
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Signature of the chiral phase transition in heavy-ion collisions. The curve labeled "mean field approximation" is the expected distribution of pions as a function of momentum perpendicular to the collision axis if a region of DCC is produced in the collision. For comparison, the other two curves are the pion distributions expected from strict adiabatic evolution from equilibrium at two different temperatures.



Particle number distributions as functions of transverse (p) and longitudinal (k_η) momentum for initial conditions corresponding to the formation of DCC (upper panels) compared with the locally thermal equilibrium number density n_i (lower panels). Notice the strong enhancements at low p and low k_η in the case where DCC is formed in the collision event.

Determination and Study of Cosmic-Ray Composition above 100 TeV

Constantine Sinnis

The origin of cosmic radiation has eluded researchers for nearly a century. The composition of cosmic rays is perhaps the single most important clue to their origin. Because of the low flux of the cosmic rays, measurements above ~ 10 TeV must be done with ground-based detectors.

We are exploring the feasibility of using a new approach to ground-based observations. We have added an experimental capability to the CYGNUS extensive air shower array

at Los Alamos to allow simultaneous ground-based measurements of (1) the Cerenkov radiation produced in a cosmic-ray-induced air shower and (2) the electron and muon densities. The Cerenkov photon density ~ 100 m from the air-shower core provides a relatively robust measurement of the cosmic-ray energy. The steepness of the lateral distribution of the Cerenkov radiation and the muon content of the air shower depend on the composition and energy.

In the past year, we successfully acquired data from a second observation period of an air shower. The new-event sample is a factor of six larger than had previously been available. Since the end of the second observation period, we have dismantled the experimental setup, and we have concentrated our effort on performing the final detailed analysis of the data and improving the shower-reconstruction algorithms. We have almost completed this work and will soon begin the final analysis of cosmic-ray composition using the combined Cerenkov, scintillator, and muon data.

At the 24th International Cosmic Ray Conference in Rome, Italy, we presented preliminary results from the first year's data.

Nonperturbative Estimates of the Standard Model Parameters

Rajan Gupta

Our project involves a comprehensive study of Standard Model physics using large-scale simulations of the underlying quantum field theory. With the advent of massively parallel computers, lattice quantum chromodynamic (QCD) calculations are reaching a quantitative and predictive level. In the past year, we finished a comprehensive analysis of standard-model phenomenology-based simulations of lattice QCD on large lattices of size $32 \times 32 \times 32 \times 64$ and with high statistical precision. We obtained and published state-of-the-art results for the hadron spectrum, meson-decay constants, semileptonic form factors, form factors for the rare decay $B \rightarrow K^* g$, and weak-matrix elements of 4-fermion operators. All these calculations were done using highly efficient computer codes on the Thinking Machines Connection Machine 5.

Results of these calculations have impact on the 4 parameters that describe the Cabibbo-Kobayashi-Maskawa mixing matrix and the 3 light quarks, i.e., on 7 of the 19 parameters of the Standard Model. Some of the highlights of our calculations include the following results:

- **Hadron Spectrum.** We obtained a detailed analysis of the chiral behavior of meson and baryon masses and the pattern of symmetry breaking for the octet and decuplet baryon states.
- **Quark Masses.** We predicted the masses of light quarks by analyzing the behavior of the masses of hadrons as a function of up, down, and strange quark masses. Our results show that these quark masses are almost a factor of 2 smaller than conventionally accepted values.
- **Semileptonic form factors for the decays $D \rightarrow K e \nu$ and $D \rightarrow K^* e \nu$.** The data is cleanest for $D \rightarrow K e \nu$ so it is used to test the pole-dominance hypothesis. By comparing the lattice result $f_+(0) = 0.66(4)$ with the present experimental values of $0.71(4)$ and $0.77(4)$, we postulate that the discretization and quenching errors in these quantities are small. For the pseudoscalar to vector decay $D \rightarrow K^* e \nu$, our result for the hard-to-measure-ratio $A_2/A_1 = 0.63(0.10)$ is in good agreement with experiments.
- **B parameters.** These parameters measure the QCD corrections to weak-interaction processes involving charge-conjugation parity (CP) violation. Our new results for the electromagnetic penguin operators suggest an enhanced value for the direct CP violation parameter e'/e .

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Biotechnology Approaches to Stable-Isotope Labeling for Biomolecular Structure/Function Studies

Jill Trehwella

A thorough understanding of biological function at the molecular level is essential for the development of new therapies to treat diseases and for an increasing array of applications in biotechnology. Knowledge of biomolecular structure is a prerequisite for understanding biomolecular function, and stable isotopes are playing an increasingly important role in the structural determination of biological macromolecules.

The application of stable isotopes is required for interpreting structural data from a variety of biophysical techniques (such as neutron scattering, nuclear magnetic resonance spectroscopy, and vibrational spectroscopies) that provide structural information down to atomic resolution. The application of these techniques to many important biochemical problems

is limited by the expense of labeling macromolecules with stable isotopes. In this project we have developed biotechnology approaches to labeling eukariotic proteins and peptides.

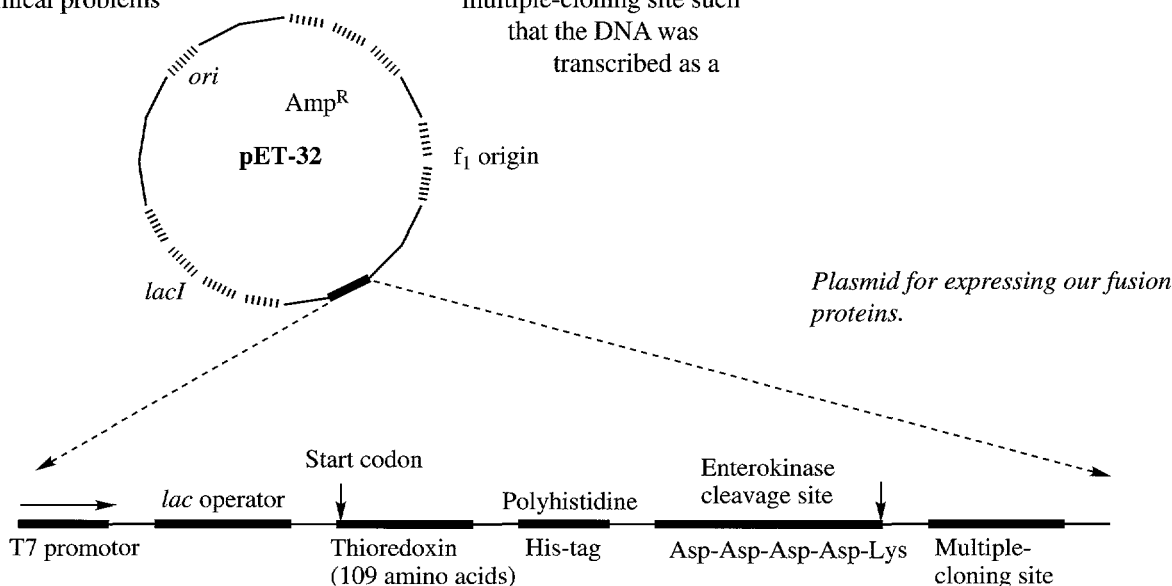
We have tested a large number of commercial bacterial expression vectors for labeling peptide fragments of troponin I (an avian muscle protein). Because peptides are subject to nonspecific proteolysis and are difficult to purify, expression of relatively small peptides in bacteria has been difficult. These problems can be circumvented by expressing peptides as a fusion with proteins that are both stable and relatively easy to purify.

In our successful plasmid construction (see accompanying figure), we cloned the DNA encoding for troponin I peptides into a multiple-cloning site such that the DNA was transcribed as a

fusion with thioredoxin, a region that encodes for polyhistidine (His-tag) and a specific protease cleavage site. Thioredoxin stabilizes the fusion protein against proteolysis. Based on the specific interaction of the His-tag region with a nickel matrix, the fusion protein is easy to purify. Finally, we liberated the troponin I peptide from the fusion protein by treating the fusion protein with enterokinase, which cleaves specifically the peptide bond to the C-terminal side of the sequence Asp-Asp-Asp-Asp-Lys.

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Preparation and Utilization of ^{13}C - and ^{15}N -Labeled DNAs for the Determination of Unusual DNA Structures Relevant to the Human Genome Project by Nuclear Magnetic Resonance Spectroscopy

Louis A. Silks

Recent reports have highlighted the involvement of DNA triplet repeats in a variety of human genetic diseases. The size and complexity of these DNA motifs necessitate the use of stable isotope labeling for structural determination by nuclear magnetic resonance (NMR) spectroscopy. We are addressing this problem by developing novel and efficient means for synthesizing these unusual DNAs, which will allow their subsequent structural determination by NMR methods. Our ultimate goal is to correlate the structure and function of these DNA motifs.

We have begun to construct DNA molecules containing triplet repeats from easily accessible precursors such as labeled methanol, carbon dioxide, and ammonia. The enzymatic synthesis of ribose (one of the components of DNA) requires carbon-labeled glycerol, so we developed a

method for synthesizing glycerol from labeled carbon dioxide and have applied for a patent on this new process. Our efforts to devise a straightforward procedure to construct 2'-Deoxy[amino- ^{15}N]Adenosine, as well as a new method for the synthesis of the unknown [9- ^{15}N]-2'-deoxyadenosine, have been reported in the literature. In short, our procedures use water as the solvent, have been scaled to provide gram quantities in excellent yield, and do not require any protection/deprotection steps.

Furthermore, we have constructed the $(\text{C}[6\text{-}^{15}\text{N}]\text{AG})_5$ repeat and optimized its purification using semi-preparative reverse-phase (C6) high-performance liquid chromatography techniques. We are currently purifying the labeled $(\text{C}[6\text{-}^{15}\text{N}]\text{AG})_5$ repeat and expect subsequent solution NMR studies to provide unambiguous evidence of the type and nature of the

hydrogen bonding to the 6-amino group on the adenines. We are also currently constructing the $(\text{C}[^{15}\text{N}_2]\text{TG})_5$ and $(\text{G}[^{15}\text{N}_3]\text{C}[^{15}\text{N}_3]\text{C})_5$ repeats to explore the bonding environments around each of the labeled nitrogens. Ultimately, these experiments will provide definitive evidence for two- or three-centered hydrogen bonding.

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Applications of Strand-Specific In Situ Hybridization

Edwin Goodwin

Fluorescence in situ hybridization (FISH) is used to determine the location of specific DNA sequences on chromosomes. A strand-specific version of FISH, called chromosomal orientation (CO)-FISH, was developed at Los Alamos. The procedure reveals not only the location but also the 5'-to-3' direction (or polarity) of a target sequence (such as the sense strand of a gene) and its orientation relative to other sequences on the same chromosome. This information is not obtainable by any other cytogenetic method.

The goal of this project is to expand the range of applications of CO-FISH. Specifically, we intend to develop methods to examine altered gene expression associated with malignancy, investigate mechanisms of gene amplification, and facilitate genomic mapping.

Using CO-FISH, we have observed long-range molecular order in the repetitive elements of tandemly repeated satellite DNAs. In addition, this year we completed our investigation of the cytogenetic phenomenon

known as lateral asymmetry, continued our investigation of aneuploidy-inducing agents, and successfully detected isochromosomes and chromosomal inversions.

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Computer Simulation of Protein Solvation, Hydrophobic Mapping, and the Oxygen Effect in Radiation Biology

Lawrence Pratt

Our work on the statistical mechanics of biomolecule solvation has widespread applications in structural and functional biology, including understanding the stabilization of folded protein structures and the binding of DNA, ligands, and other biomolecules to proteins. Our work was motivated by the need to identify hydrophobic and hydrophilic regions of biomolecules in water. The question that led to this work was, where would simple hydrophobic species such as an oxygen molecule stick to a hydrated protein? We developed theoretical molecular models of hydration (incorporating both hydrophobic and hydrophilic effects) and validated our models through computer simulations.

These new models are now available for use in structural biology studies when computer simulations are either not feasible or not insightful. They have recently been used to solve a longstanding puzzle in molecular biophysics, explaining the phenomenon of entropy convergence

in protein folding experiments. A commentary in the *Proceedings of the National Academy of Sciences U.S.A.* on our work notes that we "dramatically extend ideas" from previous theories, that our *Proc. Natl. Acad. Sci. U.S.A.* paper is a "very interesting and important paper," and that our results are "remarkable." It is clear that our work constitutes a breakthrough on these difficult problems of solvation of biological macromolecules.

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Electromagnetic Inverse Applications for Functional Brain Imaging

Charles Wood

This project addresses an important mathematical and computational problem in functional brain imaging, namely the electromagnetic "inverse problem." Two electromagnetic brain-imaging techniques, magneto- and electroencephalography, are based on measurements of magnetic fields and electrical potentials at hundreds of locations outside the human head. The inverse problem is the estimation of the locations, magnitudes, and time

sources of electrical currents in the brain from surface measurements. Although this problem is ill-posed in its most general form, approximate solutions are important for functional brain imaging used for diagnosing and treating neurological disorders and for basic research on the functional organization of the human brain.

We addressed the inverse problem using two distinct approaches: (1) introducing constraints derived from

independent information (for example, from anatomical magnetic-resonance imaging) and (2) developing new algorithmic approaches to the problem based on recent developments in large-scale numerical methods. The results suggest that we can achieve significant improvements in the accuracy and robustness of inverse solutions by these two approaches.

Publications

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Gene Shuffling Using Flow Cytometry

L. Scott Cram

We are developing a technique to engineer protein molecules with novel properties. Our technique combines the cell sorting capabilities of flow cytometry with the genetic diversity made possible through gene shuffling techniques.

Our technique is carried out in several steps. First, we create many different versions of a protein through

in vitro recombination of genes, and then we use flow cytometry to examine individual bacteria expressing the genes. Finally, we select and sort out those bacteria expressing proteins that are of particular interest using the fluorescent properties of the proteins or of other proteins in the cell that are affected by the proteins of interest. We have begun to apply this

approach to enhancing the fluorescence of a naturally occurring fluorescent protein called fluorescent green protein.

Eventually, our technique may be used to isolate proteins that turn genes on and off in response to an externally administered stimulus. In this case, we would replace the gene of interest with the gene for green fluorescent protein and monitor the conditions under which the green fluorescent protein is made.

Identification and Characterization of a Human DNA Double-Strand Break Repair Complex

David Chen

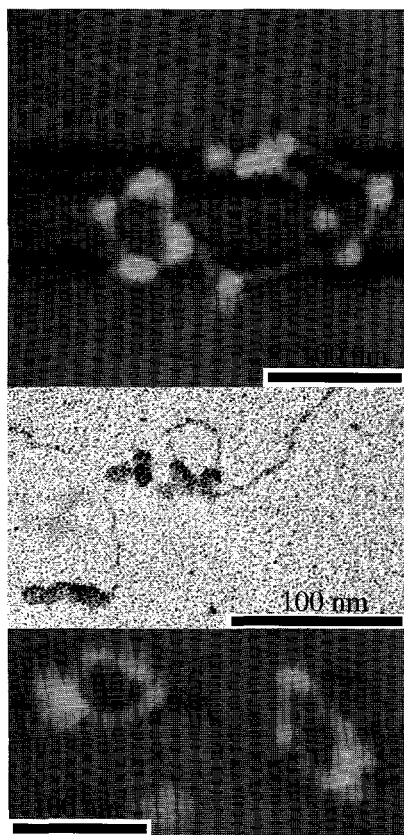
Mutations that affect the expression or activity of the subunits of the heteromeric enzyme DNA-dependent protein kinase (DNA-PK) result in

defective repair of double-stranded DNA breaks. This project studies the biochemical properties of this enzyme relevant to the repair of DNA strand breaks. This work will allow us to begin to assemble DNA double-strand break repair complexes in vitro and better understand the role of DNA-PK in the repair process.

We have successfully designed a novel purification strategy that employs

a monoclonal antibody that binds specifically to the Ku80 subunit of DNA-PK. The final product is approximately 90% pure. We employed both atomic force and electron microscopy to examine the behavior of the purified Ku70/80 and DNA-PK catalytic subunit. Direct observation of Ku/DNA complexes has shown that Ku will form nucleoprotein filaments in the presence of linear DNA. Moreover, the studies have revealed that Ku70/80 is capable of looping DNA, as the accompanying figure shows. We also used the immunoaffinity purification protocol to screen for proteins that associate with the DNA-PK complex. The most abundant protein found to associate with DNA-PK was a 120-kD polypeptide. This protein binds to DNA and is phosphorylated by purified DNA-PK.

We have used a yeast two-hybrid system for three studies: (1) mapping the domains of DNA-PK subunits involved in enzyme assembly, (2) identifying novel proteins associated with DNA-PK, and (3) identifying novel proteins associated with XRCC4, another protein that functions in the DNA double-strand break repair pathway. We designed screens of two-hybrid cDNA libraries using fragments of the catalytic subunit of DNA-PK to identify novel proteins associated with the double-strand break repair complex. The recently cloned XRCC4 cDNA has also been used in yeast two-hybrid library screens.



Atomic force microscopy (top) and electron microscopy (middle) of the Ku70/80 associated with a 2.6-kilobase-pair linear DNA fragment reveal the ability of Ku to form DNA loops. End-to-end tethering by the DNA-PK complex is shown here in atomic force micrographs of a 660-base-pair linear DNA circularized by interactions between two DNA-bound DNA-PK complexes (bottom). These results suggest that inside of the cell, DNA-PK holds broken DNA strands together until repair can occur. Micrographs provided by Robert Cary.

Determining the Role of the Telomere on the Severity of Birth Defects

Michael Altherr

The loss of genetic material near the ends, or termini, of chromosomes is associated with a variety of birth defects. Terminal deletions can arise by a variety of mechanisms, including physical breaking of chromosomes by ionizing radiation and other clastogenic agents. At least one-third of human chromosomes can have a terminal deletion but still result in a live birth, though the baby will likely exhibit significant clinical abnormalities.

Our goal is to better understand the role that telomeric sequences play in stabilizing chromosome breaks and how they affect local gene expression. Specifically, we are working to provide basic insight into the mechanism by which broken chromosomal ends are healed; to determine whether the position of the telomere to known genes can affect gene expression and contribute to the extreme variability of symptoms associated with terminal deletions; and to determine whether the position of the telomere affects local chromatin structure and in turn affects gene expression.

To meet these goals, we are mapping a chromosome region associated with a specific terminal deletion syndrome. In the past year, we have reduced the physical region thought to be involved in the Wolf-Hirschhorn syndrome to 10% of the previous estimate, and we have identified a number of genes in the missing region common to all patients with the disease.

In addition, we are using cell lines derived from patients with Wolf-Hirschhorn syndrome to examine the level of expression of cloned genes in the vicinity of the novel termini. And finally, we are employing cloned genomic material to analyze chromatin from these cell lines to identify structural variations that may affect gene expression.

Publications

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Development of an Ultrasensitive and Rapid DNA Repair Assay

Min S. Park

The main objective of this project was to develop a rapid, highly sensitive, and quantitative DNA repair assay. We expect such a kit to be useful for large-scale epidemiological studies for skin cancer risk assessment and for screening for new potential environmental mutagens. It might also be used to prescreen cancer patients who might be highly sensitive to radiation so that doctors can choose lower risk therapies.

We recognized the need for such an assay after observing that the quantity of full-size, in vitro transcripts synthesized from DNA templates decreases as a function of chemical- or radiation-induced damage to the DNA. By measuring the amount of new DNA produced after a template has been damaged, we can gauge the effectiveness of the DNA repair mechanism and better estimate the ultimate impact of the damage.

First, we studied the incorporation kinetics of nonisotopic ribonucleotide analogs in the in vitro transcription reaction and worked to optimize the use of these nonradioactive, chemiluminescent substrates. Then, we

tested the functionality of the purified DNA repair protein (XPG) using the nonradioactive substrates. Our next goal is to refine this assay so that it can be readily converted into a user-friendly DNA repair assay kit.

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Structure and Thermodynamics of Surface Recognition

Goutam Gupta

We are combining protein engineering, nuclear magnetic resonance (NMR) spectroscopy, and equilibrium and kinetic binding experiments to study the structural and thermodynamic features of HIV surface recognition—the features that enable HIV to bind to and enter susceptible cells and the features that alert the body's defenses to switch into high gear. Our goal is to identify the structural characteristics required for enhanced antigenicity, or the ability to elicit a stronger immune response.

We have targeted two well-separated sites on the HIV surface glycoprotein gp120 for our binding studies: the principal neutralizing determinant (PND) site and the CD4 receptor-binding site. For these studies we produced a set of synthetic antigens and the miniantibody/minireceptor molecules that mimic the binding affinity of the whole antibody/receptor.

Although we are primarily focusing on HIV, the methods we develop will also apply to other pathogens.

First, we chemically synthesized a series of polypeptides in which copies of the V3 region of gp120, which contains the PND site, were linked with mucin (a glycoprotein found in mucus) spacers. Using NMR and molecular modeling programs, we found that longer V3 sequences (with six mucin/V3 repeats) more readily adopted a native conformation and were structurally more ordered than those with fewer (i.e., three) repeats.

Next, we tested the antigenicity of our mucin/V3 polypeptides. However, the antisera produced by both the long and short mucin/V3 polypeptides in mice and monkeys showed no HIV neutralizing ability, which we interpreted to mean that the V3 region in native gp120 may not be as accessible as the ones in the our synthesized

mucin/V3 polypeptides, a conclusion that we have confirmed by two-dimensional (2-D) NMR structural studies on the V3 region of two strains of HIV.

Furthermore, we observed that the conserved GPGR crest in the V3 loop can be masked by the C-terminal sequence flanking the crest. In an attempt to unmask the conserved GPGR crest, we designed mini-V3 loops that contained the central 15 (out of 35) residues of the V3 loop in the S-S bridged configuration. We carried out structural studies by 2-D NMR on two such mini-V3 loops. These two mini-V3 loops adopted a rigid beta-hairpin structure in solution and unmasked the conserved GPGR crest.

Publications

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Neutron Structural Biology

Benno Schoenborn

This project investigated design concepts of neutron-scattering facilities for structural biology at spallation sources at the Los Alamos Neutron Science Center. Our work included analyzing design parameters for protein crystallography and for membrane-diffraction instruments. These instruments are designed for general use by scientists from industry, universities, and other national laboratories.

The use of large detectors will be a major component of the planned new spectrometer. For the planned

crystallographic applications, we have designed a detector with a radius of 70 cm, a height of 20 cm, and an arc of 120°. Such a detector will have a nearly 10-fold increased active area as compared with the presently used detectors. In addition to such new detectors, the new stations will use focusing optics to increase flux. The optical systems will be based on supermirror technology. We are studying further increases in flux by employing coupled moderators matched to the energy resolution required.

The completed design forms the basis for a first neutron instrument that will strengthen the local structural-biology effort and satisfy the DOE Office of Health and Environmental Research (OHER) goal to bring major diffraction tools to the scientific community. OHER has indicated that it is interested in funding these efforts in neutron structural science and supports an external-users program.

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Sum-Frequency Generation Studies of Membrane Transport Phenomena

R. Brian Dyer

Vectorial pumping of ions, generally carried out by membrane-bound proteins, is one of the most fundamental processes in living organisms, critical for energy transduction in respiration and photosynthesis and for a wide variety of cellular signal-transduction events. Because of the difficulty of obtaining structural and dynamic information on membranes and membrane-bound proteins, a molecular-level understanding of proton and ion pumping has remained elusive.

Our objective is to develop and apply a new technique, sum-frequency generation (SFG), to the study of proton and ion transport across biological membranes. Our studies

have focused on cytochrome *c* oxidase, a redox-driven transmembrane proton pump.

We have developed a nonlinear spectroscopic technique that is uniquely sensitive to membrane interfaces. Our approach uses a femtosecond titanium-sapphire laser to parametrically generate broad-band IR pulses throughout the mid-IR using the nonlinear optical materials β -barium borate and silver thiogallate. The IR pulses are combined in a nonlinear SFG process at the membrane/water interface and are detected by a multichannel SFG instrument, which we developed, that uses a spectrograph and charge-coupled device detector to detect the broad-band, up-converted IR light.

Our initial studies have focused on the water/phospholipid interface of vesicles oriented randomly in solution and on supported hybrid bilayers on fused silica. We have also worked out the biochemistry to reconstitute cytochrome *c* oxidase in liposome vesicles. We expect the combination of a carefully controlled membrane composition and structure with the structural sensitivity and interfacial specificity of the SFG technique to provide unique insight into the structures and dynamics that effect transmembrane ion transport.

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Engineering Sequence-Specific RNA and Single-Stranded-DNA Binding Proteins

Thomas Terwilliger

The technology to design a protein that binds to any given RNA or single-stranded DNA sequence has many potential applications. For example, viral diseases such as AIDS could be treated by transmitting a sequence-specific engineered protein into an infected cell, where it would bind to and inactivate a key messenger RNA. Our objective is to construct a group of protein modules, each of which recognizes a specific four-nucleotide sequence of RNA or single-stranded DNA, and then to develop the technology to link four or more of these modules in any order to generate proteins that bind specifically to any 16 (or more) nucleotide sequence of RNA or single-stranded DNA.

We have used the special properties of the gene 5 protein from bacteriophage f1 along with our experience in protein engineering to set the framework for creating a set of proteins that will bind to any specific sequence of RNA or single-stranded DNA. In the past year, we constructed a four-domain modular protein consisting of several tandem-linked gene 5 protein subunits that can be used as a template for generating a variety of sequence-specific binding proteins. By genetically linking the gene 5 protein subunits, we can design proteins in which each domain can be modified individually.

Publications

Benevides, J.M., T.C. Terwilliger, S. Vhonik, et al., "Raman Spectroscopy of the Ff Gene V Protein and Complexes with poly(dA): Non-specific DNA Recognition and Binding," *Biochem.* **35**, 9603 (1996).

Cheng, X., A.C. Harms, P.N. Goudreau, et al., "Direct Measurement of Oligonucleotide Binding Stoichiometry of Gene V Protein," *Proc. Natl. Acad. Sci USA* **93**, 7022 (1996).

Theoretical Studies of Allosteric Changes and DNA Binding of a cAMP-Dependent Transcription Activation Protein

Angel Garcia

The *E. coli* cAMP receptor protein (CRP) plays an important role in mediating transcription activation of several genes in enteric bacteria. CRP activation is a complex process involving the binding of cAMP, DNA, and RNA polymerase. Although the crystal structures of CRP with two cAMP molecules bound and complexed with DNA have been reported in the literature, a detailed understanding of the mechanism by which cAMP affects allosteric control over CRP activity remains unclear. In this project we model the structure, dynamics, and function of CRP by means of molecular dynamics simulations in aqueous and crystal environments to determine structures for CRP in different binding states of cAMP and DNA. This method will elucidate elements of the cAMP-mediated activation pathway of CRP and provide the rationale for future experimentation.

In the crystalline environment, CRP:(cAMP)₂ subunits are asymmetrically related, with one subunit in a "closed" conformation and the second subunit in an "open" conformation. The CRP:(cAMP)₂ complexed with DNA shows both subunits in a "closed" conformation. We performed molecular dynamics simulation of CRP:(cAMP)₂ in a noncrystalline environment for 625 ps in vacuum and for 140 ps in solution. We used the crystal conformation in the absence of DNA as the initial configuration. We sampled configurations during the course of the simulations and analyzed them through Molecule Optimal Dynamic Coordinate trajectories. Two optimal directions describe a transition of the "open" subunit to a "closed" subunit conformation during the first 125 ps of simulation (a subunit conformation similar to the one observed in

CRP:(cAMP)₂:DNA crystals). The simulation in solution showed that a transition from the "open" to "closed" state also occurs when water is explicitly included in the calculations. These calculations suggest that the asymmetric conformation results from lattice interactions, and that the solution conformation is similar to the symmetric (closed-closed) conformation.

Publications

Garcia, A.E., and J.G. Harman, "Simulations of CRP:(cAMP)₂ in Noncrystalline Environments Show a Subunit Transition from the *Open* to the *Closed* Conformation," *Protein Science* 5, 62-71 (1996).

Garcia, A.E., G. Hummer, and D.M. Soumpasis, "Hydration of an Alpha Helical Peptide: Comparison of Theory and MD Simulations" (to be published in *Proteins: Structure, Function and Genetics*).

Engineering the Specificity of xylR: A Bacterial Protein that Detects Chemicals in the Environment

Thomas Terwilliger

Microorganisms have sensitive systems that detect trace amounts of organic compounds; these systems are based on the ability of certain regulator proteins to bind these compounds. Binding of a compound to a regulator protein initiates a cell's response by activating the pathway to degrade that compound into nontoxic metabolites useful to the cell. In this project we manipulate the specificity of such a detector protein to produce microorganisms better able to detect and degrade organic pollutants such as trichloroethylene (TCE). Our approach is to modify the xylR protein, a regulatory protein that normally detects toluene, to detect TCE. We will determine the structure of the toluene-binding domain of the xylR protein bound to toluene using x-ray crystallographic methods, identify the parts of the protein in contact with the bound toluene, create a large number of variant proteins in which the binding surfaces are altered, and identify variants that bind TCE but not toluene using a sensitive molecular bioassay.

During the first year of this project, we have developed a system for mutagenesis and selection of xylR proteins. For efficient mutagenesis and selection of TCE-detecting variants of the xylR protein, we constructed a plasmid that contains the natural xylR gene from *P. putida* under control of an inducible production promoter. Separately, but on the same plasmid, we placed the xylR upper promoter region (which is subject to xylR control) upstream of the tetR gene, which controls the expression of tetracycline resistance. The beta lactamase gene with its promoter, which confers resistance to ampicillin, is also present on this plasmid to select for transformation into *E. coli*. This arrangement of the natural xylR gene, the xylR upper promoter, and the tetR gene yields tetracycline resistance in the presence of toluene, as the xylR protein will activate the expression of the tetR gene when toluene is present.

Optimization and Monitoring of Hollow-Fiber Bioreactors

James P. Freyer

Hollow-fiber bioreactors (HFB) are a system for culturing cells at very high densities that is currently used for the production of drugs and antibodies from mammalian cell lines. The original goals of this project were to develop novel nuclear magnetic resonance (NMR) methods for imaging transport and cellular physiology within HFB, and to use these techniques to optimize the design of HFB. To date we have developed NMR methods to measure the transport of protons (essentially water) in HFB and methods for noninvasively assaying cell viability and proliferation in specific regions of a three-dimensional culture. Unfortunately, limitations of signal strength inherent in NMR microscopy have made it impossible to measure either cellular physiology or specific nutrients within different regions of HFB.

In response to these limitations we have developed a completely novel three-dimensional cell-culture system based on essentially one-dimensional nutrient supply through a flat, porous membrane (see figure). We have noninvasively measured nutrient concentration gradients in this cell-culture system. Unlike HFB, this new system has the added advantage of being able to recover intact, viable cells from precise locations. In this way we are able to compare traditional measures of cellular physiology with noninvasive NMR measures of nutrient concentrations and cellular physiology. Thus, although the geometry is different from that employed in current HFB, the new system embodies the same relationships between the environment and the cells, but in a system that is amenable to noninvasive NMR measurement.

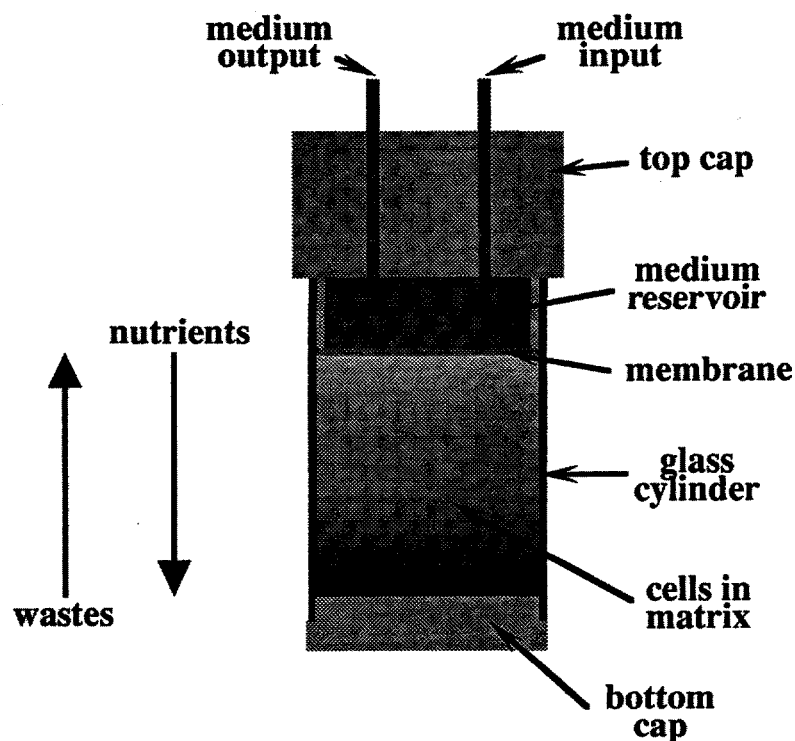
Publications

Freyer, J.P., "Mitochondrial Function of Proliferating and Quiescent Cells Isolated from Multicellular Tumor Spheroids" (to be published in *J. Cell. Physiol.*).

Kunz-Schughart, L.A., and J.P. Freyer, "Adaptation of an Automated Selective Dissociation Procedure to Multicellular Spheroids of Oncogene-Transformed Fibroblasts" (to be published in *In Vitro Cell. Dev. Biol.*).

Kunz-Schughart, L.A., R.C. Habbersett, and J.P. Freyer, "Mitochondrial Distribution and Activity in Oncogene-Transfected Rat Fibroblast Isolated from Multicellular Spheroids" (to be published in *Am. J. Physiol.:Cell. Physiol.*).

Stegman, L.D., O. Ben-Yoseph, et al., "Phosphorous MRS Evaluation of Cancer Gene Therapy Paradigm: Assessment of Ganciclovir Toxicity in Glioma Tumors Stably Expressing the Herpes Simplex Virus Thymidine Kinase Gene" (to be published in *Magn. Reson. Med.*).



A cutaway diagram along the axis of the cylinder of the new cell culture system for NMR analysis of microenvironment and physiology within three-dimensional cell-culture systems. Gradients in nutrients and waste products are established with a linear dependence on distance from the nutrient supply, as indicated on the left. The shading represents a gradient in cellular viability within the cell matrix, with viable cells (white) nearest the nutrient supply and dead cells (black) farthest from the supply.

Optimal Screening Designs for Biomedical Technology

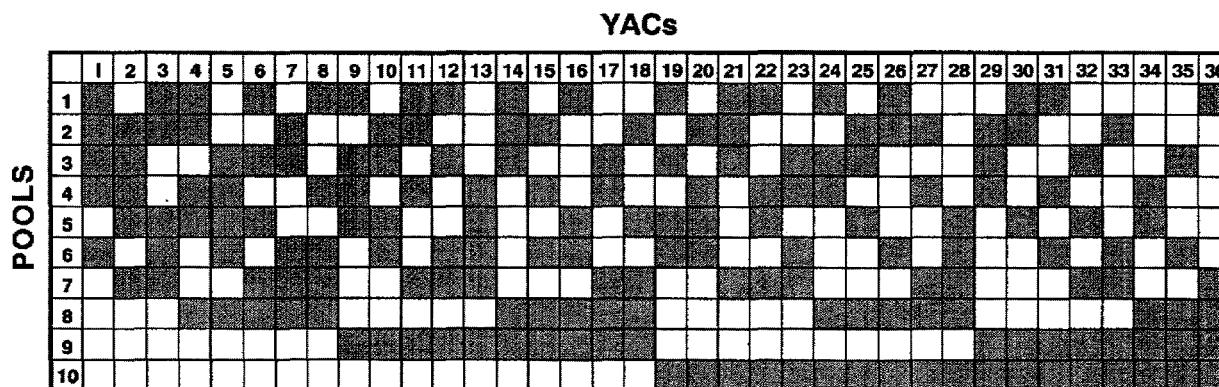
David Torney

Screening many types of molecules to isolate a few types with desirable properties is essential in biomedical technology. Unfortunately, searching for a particular molecule is often like looking for a needle in a haystack.

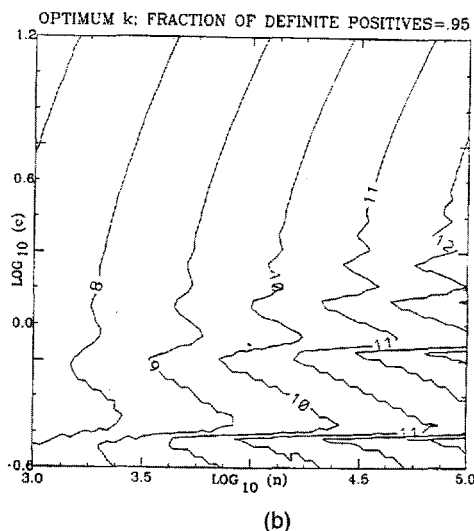
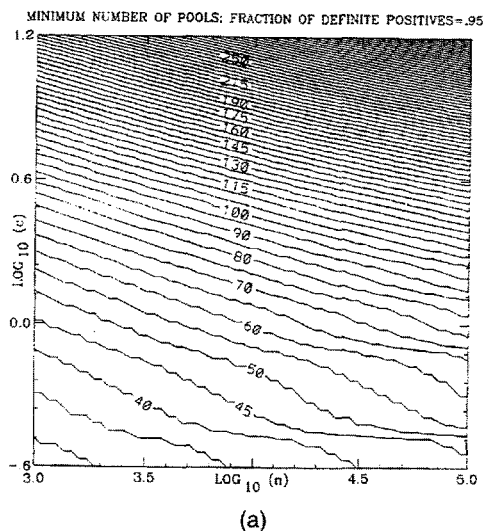
However, by testing groups or pools of molecules, the desirable molecules can be identified using a number of experiments that is proportional to the logarithm of the total number of types of molecules. The accompanying

t-design and panels illustrate the principles and practices of pooling molecules.

We are investigating efficient nonadaptive pooling designs, such as optimum random sets designs. In nonadaptive pooling designs, all pools are assigned in one pass, and all clones occur in the same number of randomly selected pools. The results of optimizing the number of pools in which each clone occurs are shown in the accompanying logarithmic plots.



This t-design depicts 36 yeast artificial chromosome (YAC) clones that we have put into 10 pools. A dark square indicates that a clone occurs in a pool. Each clone occurs in 5 pools, and each pool contains 18 clones. Assume that one of these clones is our desired "positive" product. When we test for the presence of our desired clone, we will identify the five pools containing the clone (the five positive pools). Using the information from the t-design for any four out of those five pools, we can identify our desired clone. Thus, we could identify any single positive clone even if there were a false-negative pool assay (that is, even if one of the five pools did not give a positive result, for whatever reason). This design would, however, perform poorly in the unusual circumstance that more than one of the clones is positive.



Results are plotted for clone libraries with a number of clones, n , between 10^3 and 10^5 and the average number of positive clones, c , between 0.25 and 16. It is required that the average number of definite positives (clones that must be positive) be 95% of the average number of positives. Plot (a) shows the minimum number of pools necessary to achieve this result using a random k -sets pooling design. Plot (b) shows the optimum values of k , the number of pools in which each clone should occur. Our results show the minimum number of pools that would be required based on the optimum random k -sets design.

We have applied our ideas to pool and screen clone libraries that are used in the Human Genome Project. These pooling and screening experiments required us to use liquid-transferring robots, and for the largest clone libraries, we had to adapt simpler, "row-column" pooling designs. Given the pool assay results, we developed an optimum technique for determining the probability that each clone contains the sequence of

interest. This technique works well even if there are substantial rates of errors in the pool assay data.

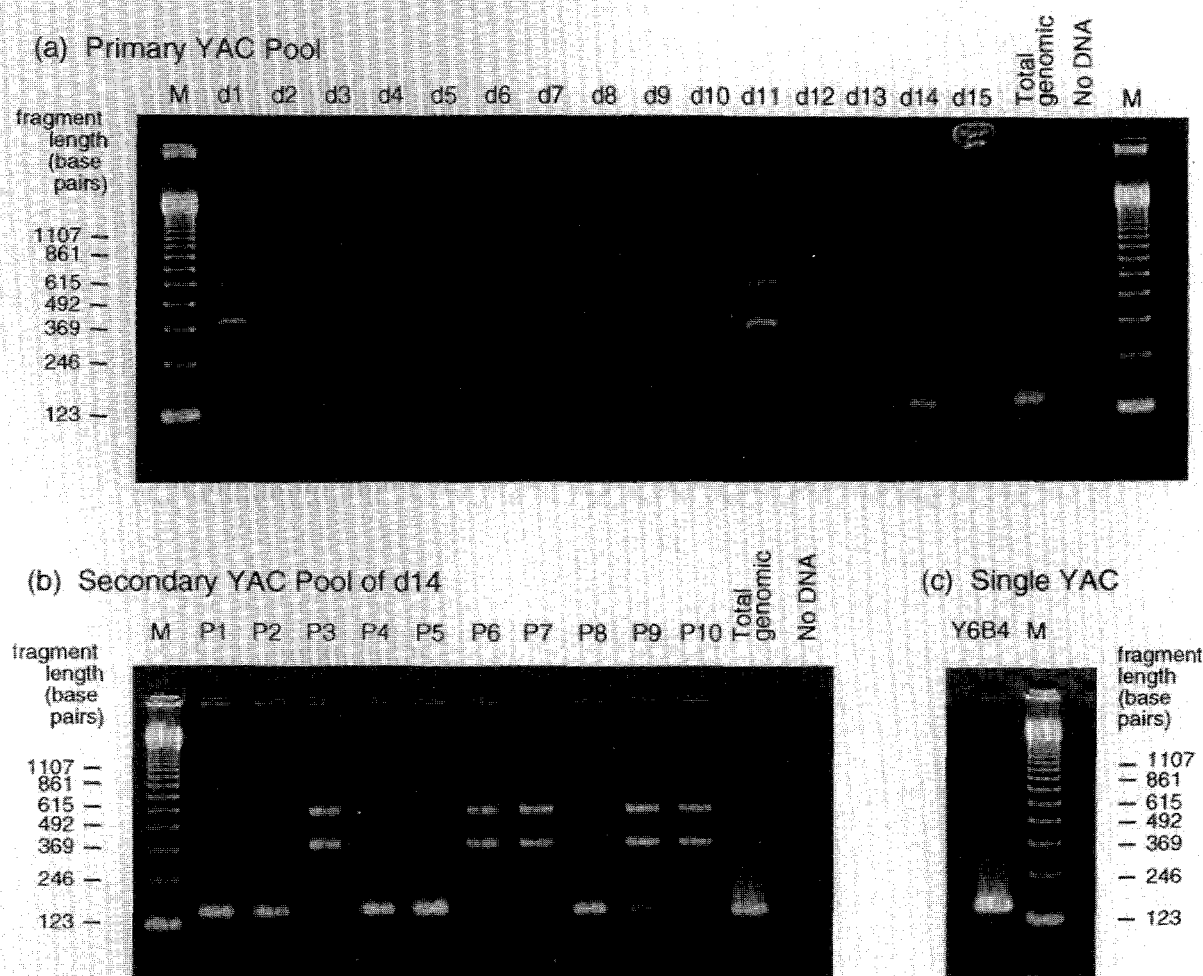
Publications

Balding, D.J., W.J. Bruno, et al., "A Comparative Survey of Non-Adaptive Pooling Designs," in *Genetic Mapping and DNA Sequencing, IMA Volumes in Mathematics* **81**, 133 (1996).

Balding, D.J., and D.C. Torney, "Optimal Pooling Designs with Error Detection," *J. Comb. Theory A* **74**, 131 (1996).

Bruno, W.J., F. Sun, and D.C. Torney, "Optimizing Non-Adaptive Group Tests for Objects with Heterogeneous Priors" (to be published in *SIAM J. Appl. Math.*).

Knill, E., A. Schliep, and D.C. Torney, "Interpretation of Pooling Experiments Using the Markov Chain Monte Carlo Method," *J. Comp. Biol.* **3**, 396 (1996).



These panels show the results of implementing the *t*-design for batches of 36 clones from a 550-clone YAC library of human chromosome 16. In panel (a), the results of polymerase chain reaction (PCR) assays are shown for 15 batches of 36 clones, denoted d1 through d15. We determined the size of the PCR products by gel electrophoresis; the desired PCR product has a size of approximately 150 base pairs. The batch denoted d14 is the only batch yielding the product. In panel (b) are the results of PCR assays of the ten pools created from the 36 clones in batch d14. These pools are denoted P1 through P10. The five pools that are positive (contain the desired PCR product) are P1, P2, P4, P5, and P8. Referring to our *t*-design (top figure, p. 124), we deduced that the positive clone should be clone 5. Panel (c) verifies that clone 5 is our desired clone. Note that the negative pools in panel (b) contain a pair of spurious bands, a frequent PCR artifact. Also, there is a trace of putative desired product in P9.

Nuclear Magnetic Resonance (NMR) Spectroscopy of Unusual DNA Structures and Functions Associated with Human Disease

E. Morton Bradbury

This work focuses on the structural biology of the insulin minisatellite, which contains a region known as the insulin-linked polymorphic region (ILPR) that is associated with insulin-dependent diabetes mellitus. The human insulin minisatellite is located upstream of the insulin gene and its length is highly polymorphic.

We have performed two-dimensional NMR spectroscopy, gel electrophoresis, digestion by single-strand-specific P1 nuclease, and in vitro replication to determine the

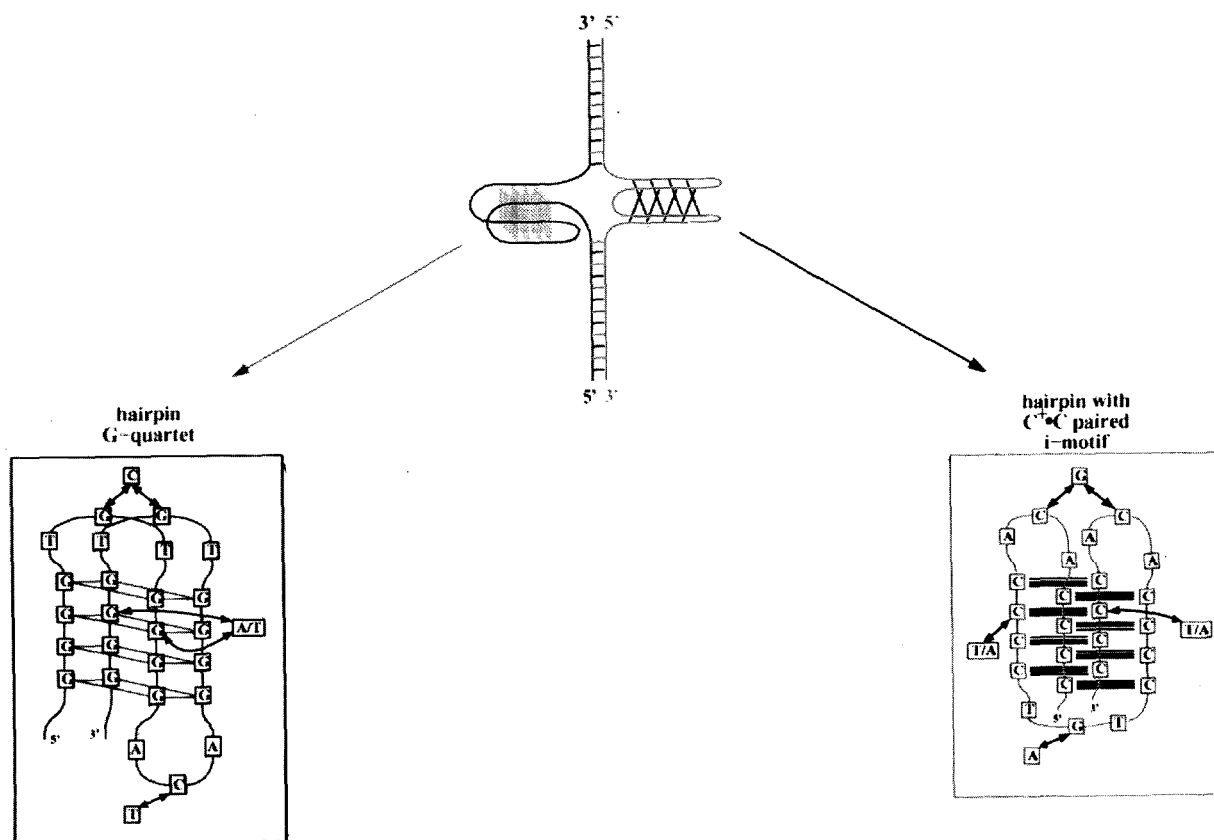
structure of the human insulin minisatellite. Our efforts have focused on a region of the ILPR in which one strand is rich in guanine (G) and the other in cytosine (C).

We have shown that the G-rich strand adopts a hairpin G-quartet structure, whereas the C-rich strand adopts an intercalated C+•C paired i-motif structure (see accompanying figure). Formation of these structures causes slippage during replication, which might contribute to the observed length polymorphism.

Formation of these structures also causes unwinding (and negative supercoiling) upstream of the transcription start site, which may facilitate transcription. We also found that single-site mutations that disrupt the stem or loop structure of the hairpin G-quartet or the C+•C paired i-motif reduce the transcriptional activity of the insulin gene and that two or more site mutations block all transcriptional activity. These results support our hypothesis that the structures of the hairpin G-quartet and the C+•C paired i-motif regulate transcription of the insulin gene.

Publications

Catasti, P., X. Chen, R.K. Moyzis, et al., "Structure-Function Correlations of the Insulin-Linked Polymorphic Region," *J. Mol. Biol.* **264**, 534 (1996).



A schematic representation of the structure of the multiple hairpin G-quartets and the C+•C paired i-motif.

Emerging Pathogens: Dynamics, Mutation, and Drug Resistance

Alan Perelson, Los Alamos National Laboratory
Frederick G. Hayden, University of Virginia

Pathogens that can grow rapidly and mutate into drug-resistant forms pose a serious health threat. One such pathogen, influenza, is one of the world's greatest killers. In a normal "flu" season, between 20,000 and 40,000 deaths in the United States are attributable to influenza infection, and in the 1918–1919 pandemic, over 21 million people died worldwide. Two antiviral drugs, amantadine and rimantadine, are currently available and in limited use against influenza infection; their use should prevent such large numbers of deaths if another pandemic strikes.

However, before large-scale treatment programs are begun, as might occur with a major outbreak or pandemic, the health significance of potential drug-resistant viruses must be addressed. Furthermore, treatment strategies must keep emergence of drug-resistant strains at reasonably low levels and still permit treatment of infected individuals. (Researchers designing countermeasures to biological agents released during warfare or by terrorist activities address similar public health issues.)

The goal of this project is to consider strategies to reduce the severity of an ongoing biological

threat without compromising our future ability to respond to the same threat because of the emergence of drug-resistant pathogens. To this end, we have developed a quantitative model that describes the spread of one infectious pathogen, influenza. We have fitted our model to data on one outbreak of influenza and found excellent agreement.

Our model suggests that large-scale treatment of individuals once they become sick readily generates drug-resistant variants. Prophylaxis, a strategy in which individuals are given drug treatment before they become sick, leads to lower levels of infection and, hence, lower emergence of drug-resistant variants. Because our model's predictions depend on how we assessed various parameters, extending our results to other pathogens will require detailed knowledge on the spread of the disease and the effects of treatment.

Optical Measurement of Drug Concentrations in Tissue

Irving Bigio

The goal of this project is to develop noninvasive fiber-optic methods for measuring drug concentrations (specifically, chemotherapeutic drugs) in tissue. Such a capability would greatly benefit the study of chemotherapy drug kinetics (i.e., the time dependence of drug concentrations) at specific targeted locations in the body after a drug has been administered. Our specific objective is to develop a general method for measuring the concentrations of optically absorbing compounds in turbid media by circumventing the problems caused by scattering.

We performed Monte Carlo simulations of photon transport to determine optimal fiber spacings and fiber sizes for measuring absorbance in highly scattering media such as tissue. Based on the results of the Monte Carlo simulations, we designed and constructed fiber-optic probes and used them to take measurements on a variety of tissue phantoms (materials with optical properties similar to those of tissue). We also developed a technique for measuring changes in absorption in a medium with unknown scattering properties, and we tested our new technique on media with scattering

properties similar to those of tissue. We were able to measure concentration changes of an added absorber similar to what might be expected for drugs at typical therapeutic doses. The results of this work have been submitted to *Applied Optics* for publication.

Finally, we measured the absorbance of some chemotherapeutic drugs to determine whether they have absorption bands in a wavelength range feasible for absorbance measurements in tissue.

Publications

J.R. Mourant, I.J. Bigio, D.A. Jack, et al., "Measuring Absorption Coefficients in Small Volumes of Highly Scattering Media: Source-Detector Separations for which Path Lengths Do Not Depend on Scattering Properties" (submitted to *Applied Optics*).

Stable-Isotope Labeling of Oligosaccharide Cell-Surface Antigens for Structural Studies

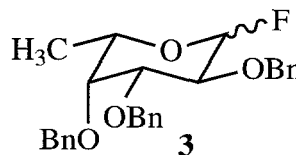
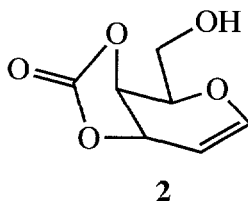
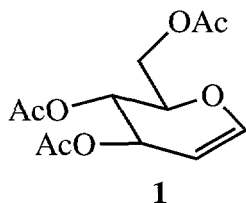
Clifford Unkefer

The cellular envelopes of many types of animal cells are coated with oligosaccharides that are involved in important processes such as cell-cell recognition and adhesion. In addition, oligosaccharides are capable of eliciting immune responses and differentiating, for example, the blood groups (A, B, AB, and O). Cell-surface oligosaccharides are also recognized by and serve as receptors for many infectious agents, including viruses and bacterial toxins.

All of these functions of oligosaccharides involve the specific binding of the cell-surface oligosaccharide by a protein molecule. The design of pharmaceutical agents that can specifically inhibit the binding of a bacterial toxin to an oligosaccharide receptor would be greatly facilitated by knowledge of the conformation of both the free and bound forms of the oligosaccharide. Advancing our understanding of the conformation of oligosaccharides is dependent on the application of methods such as nuclear magnetic resonance (NMR) for determining their structures. As has been demonstrated in the NMR analysis of protein structures, stable-isotope labeling is required for increasing spectral resolution and assigning the resonances. At present it is not possible to label most oligosaccharides with ^{13}C .

Because most of the interesting oligosaccharide structures derive from mammalian sources, biochemical approaches to labeling them are impossible. Recently, Danishefsky and coworkers at Slone Kettering Cancer Center developed a method for the solid-phase chemical synthesis of oligosaccharides. The goal of our LDRD project was to prepare uniformly ^{13}C -labeled aldohexose precursors required for the solid-phase synthesis of the Lewis blood-group antigenic determinants.

The solid-phase synthesis of the Lewis oligosaccharides required three precursors: a D-glucose or N-acetyl-D-glucosamine precursor (1), a D-galactose precursor (2), and an L-fucose precursor (3). These precursors are shown in the accompanying figure. Compounds 1 and 2 contain three asymmetric centers (C3–C5); compound 3 contains four asymmetric centers (C2–C5). Using uniformly ^{13}C -enriched D-glucose as a chiral precursor, we have prepared 1, 2, and 3 in good yield. In two steps we converted D-[U- $^{13}\text{C}_6$]glucose to 1; the stereochemistry at C3, C4, and C5 is retained. Synthesis of 2 required the inversion of the center at C4. The conversion of D-glucose to L-fucose required the inversion of three asymmetric centers (C2, C3, and C5).



The precursors that we used in our solid-phase synthesis of the Lewis oligosaccharides (Ac is an acetyl group, and Bn is a benzyl group). Compound (1) is the precursor of D-glucose and N-acetyl-D-glucosamine, (2) is the precursor of D-galactose, and (3) is the precursor of L-fucose.

We are presently collaborating with the Danishefsky group on the synthesis of the Lewis oligosaccharides and the NMR analysis of their solution conformation.

Publications

Lodwig, S.N., and C.J. Unkefer, "Stereoselective Synthesis of Stable Isotope-Labeled L- α -Amino Acids: Electrophilic Amination of Oppolzer's Acyl Sultams in the Synthesis of L-[^{15}N]Alanine, L-[^{15}N]Valine, L-[^{15}N]Leucine, L-[^{15}N]Phenylalanine and L-[1- ^{13}C , ^{15}N]Valine," *J. Labelled Compounds and Radiopharmaceuticals* **38**, 239 (1996).

Lodwig, S.N., L.A. Silks III, and C.J. Unkefer, "Synthesis of 1-Chloro-1-[^{15}N]Nitrosocyclohexane: an Electrophilic Aminating Reagent," *J. Labelled Compounds and Radiopharmaceuticals* **38**, 161 (1996).

Oppenheimer, J., and L.A. Silks III, "Synthesis of 2-Phenyl-1,2-benziso[^{77}Se]selenazol-3(2H)-one; 'Ebselen,'" *J. Labelled Compounds and Radiopharmaceuticals* **38**, 281 (1996).

Orji, C.C., J. Kelly, et al., "The First Synthesis of [9- ^{15}N]-2'-Deoxyadenosine," *J. Chem. Soc., Perkin Trans. 1* **7**, 595 (1996).

Wu, R., and L.A. Silks III, "Synthesis of D-[1,2,3,4,5,6- $^{13}\text{C}_6$]Glucal and D-[1,2,3,4,5,6- $^{13}\text{C}_6$]Galactal Using D-[U- $^{13}\text{C}_6$]Glucose as the Sole Carbon Source" (submitted to *Carbohydr. Res.*).

Protein Motions that Determine the Efficiency of Photosynthesis

Joel R. Berendzen

In this project our goal is to understand the quantum efficiency of biomolecular photocells. Achieving this goal requires that we combine x-ray crystallography at cryogenic temperatures with theoretical calculations to determine the structure of reaction centers under illumination and understand the changes in protein structure that occur upon charge transfer. These structural changes are thought to be responsible for the remarkable quantum efficiency (greater than 98%) of these cells. Understanding them could help to answer fundamental questions about

energy transduction in the reaction center, including the role that the various pigments and protein domains play in preventing the unwanted "back" reaction.

We have made substantial progress toward our goal. We have attracted the collaboration of Nobel Prize winner Hartmut Michel's group at the Max-Planck Institute for Biophysics, Frankfurt, Germany, in carrying out the crystallography. We constructed a novel instrument, an ultraviolet-visible (UV-VIS) absorption spectrum microspectrophotometer, designed for on-line operation at a synchrotron to

measure the absorbance spectra of reaction center crystals and carry out photoactivation. We have obtained the first-ever data set for a reaction center crystal at cryogenic temperatures, and it diffracts well. In collaboration with the National Institutes of Health, we have developed methods that allow accurate and efficient calculations of free-energy differences from simulations of equilibrium states. These methods will enable examination of electron-transfer mechanisms. We have also developed an electron-transfer pathway analysis program based on a tree search that can find the 100 best electron-transfer pathways in a small protein (such as cytochrome *c* with 1700 atoms) in just a few seconds on a desktop workstation. We will use this tool to analyze differences in pathways before and after illumination.

Studying Properties of Cell Suspensions with Elastic Scattering

Irving Bigio

Cancer diagnosis is commonly verified with surgical biopsies followed by pathology assessment, an invasive and time-consuming procedure. Optical techniques for non-invasive tissue diagnosis are now being developed, offering significant advantages over standard biopsy and cytology techniques, both in terms of patient care and medical costs.

In previous work using elastic-scattering spectroscopy to detect cancer, we obtained sensitivities and specificities in the upper-90th percentile range for some forms of

cancer of the bladder and colon.

These results were obtained empirically without a detailed understanding of the sources of the spectral differences. The purpose of this project was to study suspensions of cancerous and noncancerous cells in order to determine the cause of the spectral changes.

We have made measurements on M1, MR1, RAT1, and RAT1-T1 cells, which are derived from the same line of normal rat fibroblast cells. The MR1 and RAT1-T1 cells are capable of forming a tumor while the others

are not. We found repeatable differences in light scattering properties of the M1 and MR1 cells; however, the data on the RAT1 and RAT1-T1 cells is still inconclusive. Our preliminary evidence suggests that the growth stage of the cells affects the scattering. We also developed two new methods for estimating the size of the scatterers in highly scattering media and have determined that the predominant scattering centers average only 0.3 microns in diameter.

Publications

J.R. Mourant, J.P. Freyer, and T.M. Johnson, "Measurements of Scattering and Absorption in Mammalian Cell Suspensions," *SPIE Proc.* **2679**, 79-84 (1996).

Numerical Simulations of Biochemical Self-Organization: Calcium Wave Propagation and Microtubule Growth

John Pearson

We are investigating the calcium fertilization wave in xenopus eggs and microtubule dynamics. These issues are treated separately, although we intend ultimately to couple the calcium dynamics with the microtubule dynamics to create a plausible numerical model of mitosis. We are also working to elucidate the differences between the mature and immature oocytes.

We have developed both particle and mean-field models of microtubule dynamics that reinforce our preliminary result that the generic behavior of tubelike objects is to form clumps of growing tubes separated by empty regions. The separation between clumps is apparently determined by the rate of tubulin diffusion and of the binding constants.

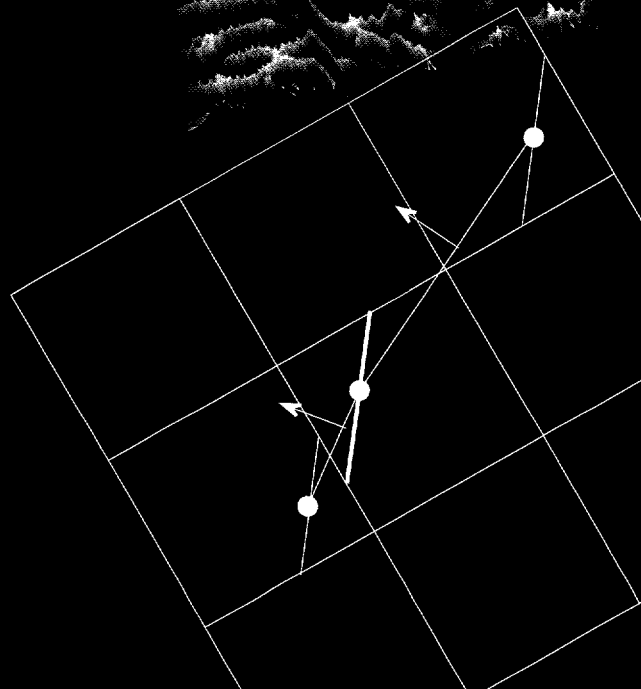
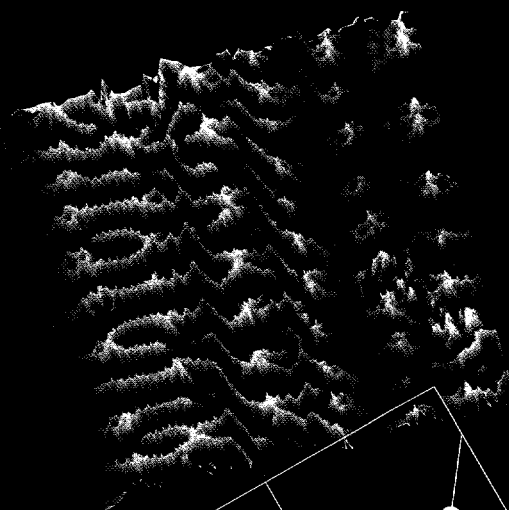
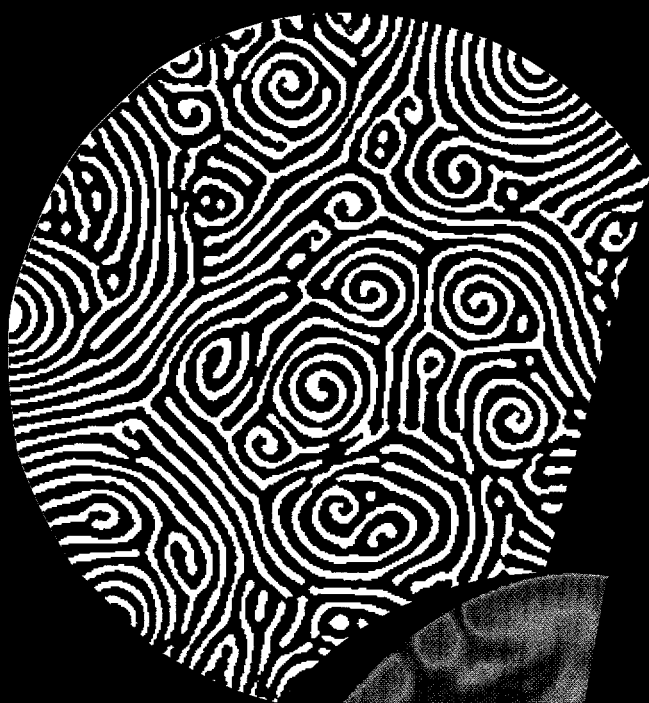
We have developed computer codes for simulating the nonlinear dynamics of the calcium wave propagation. These codes are in one, two, and three dimensions. We have performed a detailed analysis of the traveling wave solutions in one dimension of the nonlinear dynamical. This analysis will be used as a guide in performing numerical simulations in the more realistic two- and three-dimensional models. This involves the numerical continuation of the traveling wave solutions of the de Young-Keizer model as parameters are varied. It turns out that there are over a dozen parameters that are not well known in the case of the mature oocyte. We have extended our numerical models to account for a nonuniform distribution of the endoplasmic reticulum, and we have begun the exploration of the effects of the endoplasmic reticulum distribution in the spherical oocyte.

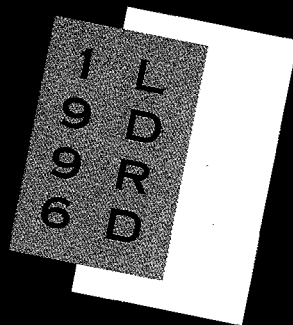
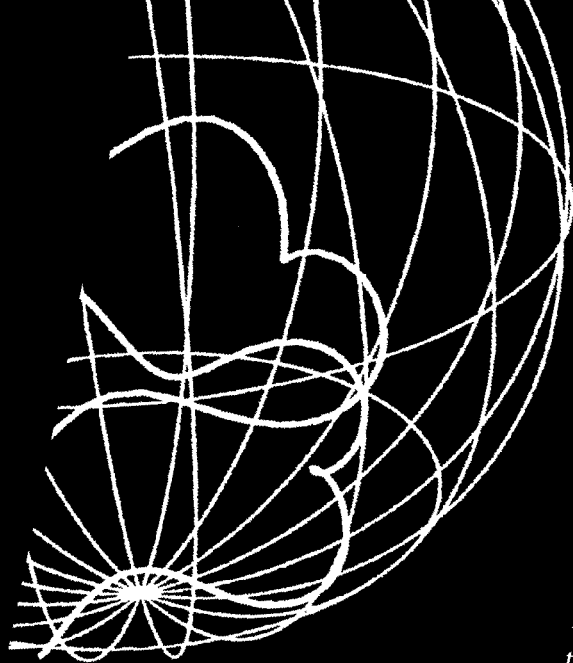
We have developed both mean-field models and a particle model for the dynamics of microtubulelike objects in two space dimensions. To perform ensemble averages of the particle dynamics, we have ported our code to the massively parallel Cray T3D, thus generating several hundred realizations. The clumping phenomenon observed in the particle simulations was also observed in the mean-field model. We performed a crude analytical calculation on the mean-field model that indicates such clumping should be expected. We have also developed mean-field models for the dynamics of tubes with tail dynamics but these remain to be explored.

Publications

Reynolds, W., S. Ponce-Dawson, and J. Pearson, "Self-Replicating Spots" (to be published in *Phys. Rev. E*).

Baras, F., M. Mansour, and J. Pearson, "Microscopic Simulation of Chemical Bistability of Homogenous Systems," *J. Chem. Phys.* **105** (18), 8257 (1996).





Competency Development Projects

Competency Development (CD) projects support management-initiated R&D in new areas that will stretch—not just maintain—the Laboratory's core competencies. These competencies, which grew out of our historical mission of developing and maintaining the nation's nuclear deterrent, include nuclear weapons science and technology; complex experimentation and measurement; nuclear and advanced materials; theory, modeling, and high-performance computing; analysis and assessment; earth and environmental systems; and bioscience and biotechnology. This year, CD projects accounted for 37% of the LDRD budget and 33% of all projects, and they supported research in eight of the nine technical disciplines.

Examples of subjects investigated by CD projects include foreign nuclear test radiochemical diagnostics; dynamic, high-strain deformation of materials; remote-sensing science; structural and magnetic characterization of actinide materials; advanced computational science; adaptive Monte Carlo methods for radiation transport; magnetized target fusion; and the structure, dynamics, and function of biomolecules.

Actinide Crystal Structures with an Emphasis on Plutonium Alloys

Joyce Roberts

Complexity of crystal structure is the outstanding scientific problem of actinide crystal chemistry. We do not know why the idiosyncratic structures of plutonium metal occur, and we do not know how they transform among themselves. The electronic instability of the 5f electronic shell that is just beginning to be filled in the light actinides causes "self-intermetallic" compounds (in which the same element is in more than one valence state or crystallographic site) to be formed in both plutonium metal and its alloys, and the formation of these compounds is responsible for the observed complexity of structure and phase behavior.

The goal of this project is to contribute to an understanding of this complexity by determining the crystal structures of several actinide alloys: Np-U, Pu-Th, and Pu-Zr. It is our intention that this additional structural data will eventually lead to a solution of the plutonium structure problem. The ultimate goal of this research is to understand the complex phases of plutonium and the interrelations between them.

During the past year we made progress in the following areas: (1) We are establishing new sample-preparation facilities, and these facilities are nearly complete. (2) We spent several weeks on an unsuccessful attempt to index our neutron data from the eta-phase in the Pu-Np and Pu-U systems. Although we have not yet indexed this structure, this attempt has eliminated several blind alleys and will contribute to the eventual success of this effort. (3) We performed low-temperature characterization of zeta-phase Pu-U

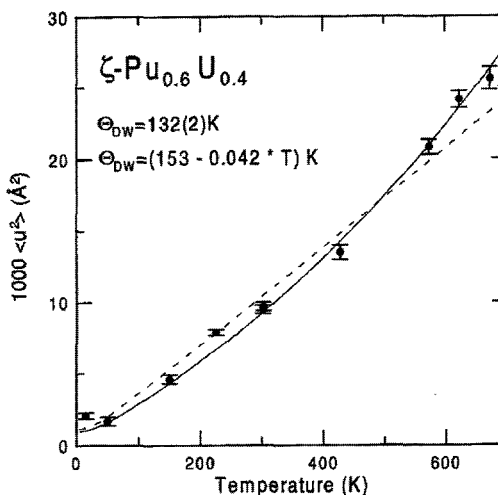
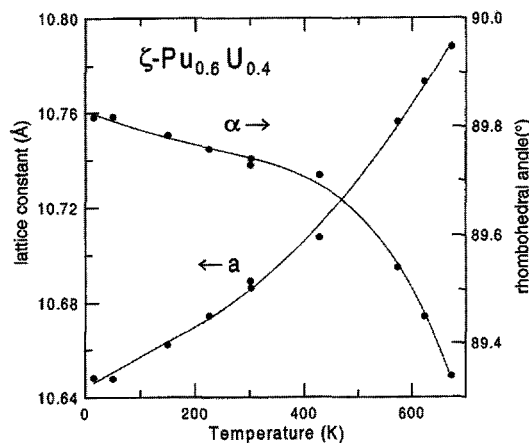
using neutron diffraction. We observed that the rhombohedral angle approaches 90° more closely than it did in our previous high-temperature experiments, but that no further transformations take place (see plot of lattice constants vs temperature). Completing the low-temperature measurements allowed us to extend our analysis of the Debye-Waller temperature (a characteristic parameter

of a solid that measures the sound velocity). An anharmonic model that allows the Debye-Waller temperature to vary with temperature provided a better fit to the data than a simple Debye-Waller model (see plot of average mean-square displacements vs temperature). This outcome is consistent with our results from the light actinides.

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Rhombohedral lattice constants vs temperature for the zeta-phase Pu-U (α is the rhombohedral angle, and a is the lattice constant). During this study we added data taken below room temperature to our previous data taken above room temperature. Error bars are smaller than the plotted points.



Mean-square thermal displacements of the atoms isotropically averaged over all crystallographic directions for the zeta-phase Pu-U vs temperature. The solid line is the anharmonic mode (in which the Debye-Waller temperature varies with temperature) fit to these data. The simple Debye-Waller model is given by the dashed line.

The Implications of Diffraction In Situ Loading Macrostrain Measurements in Composites and Finite-Element Interpretations

Ning Shi

The morphology of the evolution of elastic macrostrain can be affected by different physical processes, such as matrix plastic and creep flow and reinforcement fracture. The onset of these processes sometimes cannot be readily detected by conventional methods. We are using neutron-diffraction, in situ loading measurements, and finite-element analysis to understand the evolution of the elastic macrostrain in composites with the objective of enabling nondestructive assessment of internal damage. In addition, we are studying the effect of in situ creep on the load sharing between phases during isostress loading.

We have measured the dislocation density and thermal residual elastic strains in NiAl reinforced by 20 vol % Al_2O_3 particulates. As the size of the reinforcement increases, the average dislocation density increases and the corresponding thermal residual elastic strain decreases, as shown in the first figure. The changes with respect to particle size in the dislocation density

and residual strain can be explained neither by continuum theory nor by continuum-based dislocation mechanics. This disagreement can be explained by the fact that insufficient independent slip systems in NiAl hinder plastic relaxation in individual grains when embedded into a crystal aggregate because of the constraints by neighboring grains. As the particle size increases, a greater number of grains participate in the relaxation process, and a collaborative slip among grains eases the constraints. That is, as the neighboring grains slip, each individual grain does not have "rigid" surroundings. This model is supported by the polycrystalline plasticity calculations.

The second figure is from a two-dimensional (2-D) crystal-plasticity calculation and shows that the total amount of slip stays almost unchanged relative to the particle size when the matrix possesses a sufficient number of slip systems (three independent slip systems are sufficient for 2-D). As the number of

independent slip systems reduces to one, the amount of slip increases with the particle size, in line with the experiment and the model.

Publications

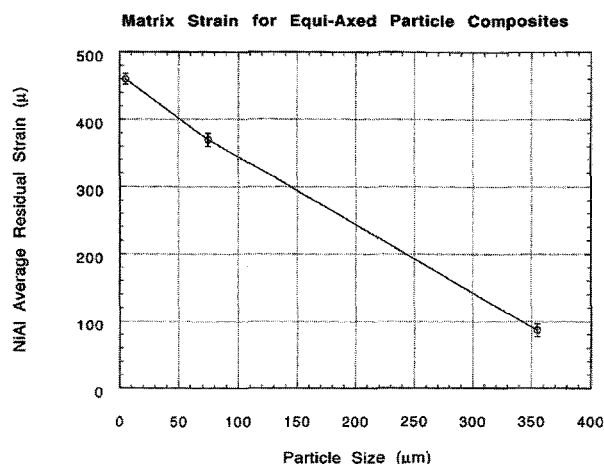
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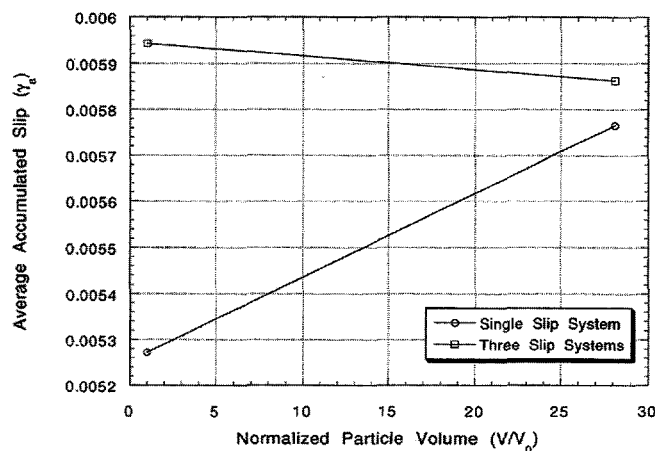
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Measured NiAl thermal residual strain as a function of reinforcement size.



Calculated average accumulated slip vs normalized individual particle volume. A comparison of single- and three-slip systems.

Chemical and Physicochemical Properties of Submicron Aerosol Agglomerates

Ronald Scripsick

Nanometer-sized aerosol particles are a by-product of high-thermal-energy processes including waste incineration and explosions. They may also be intentionally generated for use as superconducting powders and ultraviolet screening films. This research focuses on the chemical properties of nanometer particles and their agglomerates.

In previous experiments we generated binary aerosol mixtures of zinc oxide with magnesium oxide and of copper oxide with magnesium oxide from aqueous solutions of metal salts. We atomized, dried, and passed them through a flat flame burner. We found the agglomerate-particle mass distribution with respect to aerodynamic diameter to be bimodal for the zinc and magnesium in the ZnO/MgO system. In the CuO/MgO system, the magnesium distribution was bimodal and the copper was concentrated in the smallest size ranges (particle diameter < 0.5 micron). The bimodal size-distribution of the aerosol

suggests that two simultaneous pathways exist to metal-oxide aerosol formation from solid-phase, metal-salt precursors: (1) vaporization and chemical reaction followed by gas-to-particle conversion, and (2) solid-phase reaction to the oxide.

Recent focus has been on the gas-to-particle pathway to aerosol formation. In order to study the effect of precursor chemistry on particle-composition heterogeneity, we generated mixed SiO₂/TiO₂ aerosol in a flat flame burner from three sets of gas-phase precursors: SiBr₄/TiCl₄, SiCl₄/TiCl₄, and hexamethyldisiloxane (HMDS)/TiCl₄. We found SiO₂/TiO₂ an interesting system because no mixed phase exists, nor is there any thermodynamically stable solubility of SiO₂ in TiO₂ in the solid phase.

We developed techniques to determine the scale of mixing using transmission electron microscopy/energy-dispersive spectroscopy (TEM/EDS) and scanning transmission electron

microscopy/energy electron loss spectroscopy (STEM/EELS). For all combinations of precursors, TEM/EDS revealed little variation in composition from particle to particle. The homogeneity from particle to particle suggests that chemical reactions of the precursors to form the condensable species are occurring simultaneously, and any differences in chemical reaction behavior of the precursors are insignificant. The segregation within the particles is probably occurring by solid-state diffusion during particle formation as a result of the immiscibility of the two oxide species.

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Characterization of Bioactive Materials Using Neutron Reflectivity and Atomic Force Microscopy

Gregory Smith

The objective of this project is to apply neutron reflectivity and atomic force microscopy to characterize the structure and phase behavior, the interlayer and intermacromolecular interactions, and the protein shape stability of a fundamentally new class of bioactive molecular systems. This system is composed of reconstituted and native self-assembled membrane proteins complexed with associating and surfactant polymers.

This year we have prepared oriented films of the lipid DMPC on silicon substrates. However, these films have not proved to be ideal for these studies. Although the films initially form well-oriented samples, they delaminate from the substrates upon hydration.

Our major accomplishment this year was to design and construct a controlled-humidity oven that can be used for producing oriented, freely

suspended films of lipid multilayers. Because these films are 5 cm × 5 cm in area, they are appropriate for our neutron-reflectivity studies. We also began testing of the oven, and we have designed and are currently constructing a new constant-humidity control system for use with the oven. We expect to begin a series of experiments with simple lipid membranes first and then lipids with DNA, polyethylene glycol lipid, or lipoproteins.

Bulk Amorphous Materials

Ricardo B. Schwarz

Bulk amorphous metallic alloys (also known as "bulk metallic glasses") are strong, corrosion-resistant materials that can be cast in near-net-shape form by techniques such as injection molding. Because of these characteristics, bulk metallic glasses are used to make such equipment as gears (especially complicated shapes that are difficult to machine), surgical tools, corrosion-resistant parts such as valves, and seamless tubes.

The broad goal of our project is to develop novel materials with potential for industrial or defense applications. We are developing methods to synthesize and characterize bulk metallic glasses and multiphase metastable alloys formed by mechanical alloying. We are researching the conditions for forming these alloys and the basic properties of the alloys, including thermal stability, mechanical properties, and hydrogen storage characteristics. Another goal of our research is to develop bulk magnetic glassy materials. Currently, no such materials exist, but the discovery of bulk magnetic metallic glasses would lead to a tremendous energy savings nationwide.

This year we have achieved the following:

1. **Improvement in the Synthesis Techniques.** We improved a melt-fluxing technique that we had developed last year. This technique enables us to produce 1-in.-diam rods of amorphous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, the largest rod of this material ever produced (see accompanying figure). A patent application for this method is being processed by the Laboratory.
2. **New Alloy Compositions.** Previously, bulk amorphous Pd-Ni-P alloys were only known at the composition of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$. This year, we were able to cast amorphous alloys containing only 25 at. % of palladium in the form

of 10-mm-diam rods. Being able to use less palladium represents a significant reduction in the cost of these alloys. We have also discovered the formation of bulk amorphous alloys in Pd-Cu-P and Pd-Ni-Fe-P systems.

3. **Collaborations with Other National Laboratories.** We have supplied samples of our alloys to other national laboratories and universities to establish collaborative work using their unique facilities and expertise (corrosion studies at Brookhaven National Laboratory; structure determination at the National Synchrotron Light Source, Brookhaven; and atom probe microscopy at Oak Ridge).
4. **Metal-Ceramic Composite Powders.** In another phase of our research, we are using mechanical alloying—a high-energy ball-milling technique—to prepare metal-ceramic composite powders from vanadium oxide, magnesium, and aluminum powders. The fine-grained powders that we produce by this method are quite resistant to mechanical degradation in hostile radiation environments and do not crack as easily as the corresponding large-grain powders

produced by other preparation methods.

Publications

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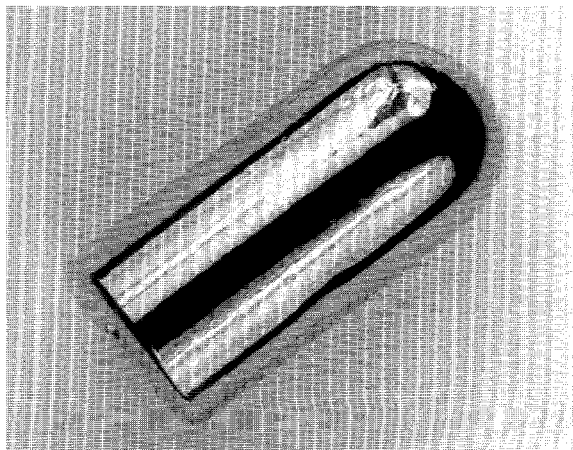
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Characterization of Advanced Electronic Materials

Joe D. Thompson

The ability to characterize (measure and interpret) properties of advanced electronic materials bridges the gap between materials synthesis and theoretical modeling. This project builds on and extends the Laboratory's competency in nuclear and advanced materials by characterizing the ground states of materials in which electronic correlations dominate the materials' properties. Our goal is to discover new physics by understanding the complex interplay among microscopic interactions that produce these ground states.

This year we have discovered evidence for an unexpected form of magnetism that develops in the superconducting state of B-doped UBe₁₃. We also used a broad range of experimental techniques to study the evolution of a first-order, isostructural valence transition with silver substitution in YbIn_{1-x}Ag_xCu₄ and found that interactions driving this transition are played out on the unit-cell scale. Scaling analysis of thermodynamic data established that gaps in the spin-

and charge-excitation spectra of a correlation-driven semiconductor obey different functional dependences. Analysis of the competition between magnetic and electronic interactions for the ground states of several rare-earth and actinide intermetallic compounds has been made.

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Neutron Scattering Studies on Shear-Induced Structure in Polymers

Rex Hjelm

Our objective is to study polymer-surface interactions and shear-induced, polymer orientation in the bulk. These aspects include self-lubrication effects in polymers under flow- and shear-induced phase transitions in liquid crystal polymers. Shear is introduced in industrial processing when a polymer melt or concentrated solution is passed through an orifice, such as a spinner used in fiber formation, or by injection into the mold used in injection

molding. Thus the production of fibers and molded parts in industrial applications naturally introduces flow shear, which affects the conformation and orientation of polymer chains, making the effects of shear on polymer conformation and orientation of considerable industrial interest. A detailed understanding of the physics of polymers under shear that could be used to connect the structure of polymers with their unique rheological properties has yet to emerge. Thus

there is little basis for predicting the effect of an industrial processing strategy on material properties.

The task for this year was to design and construct the apparatus needed for this project. This work included completion of an improved Couette-geometry shear-cell rig with better thermal isolation and control and better shear-cell alignment characteristics as well as fabrication of aluminum, Couette-geometry shear cells for high-temperature shear work. We also designed a cone and plate rheometer for neutron reflectometry experiments. We prepared materials to study shear flow characteristics of liquid crystal polymers for measurements planned for early next year.

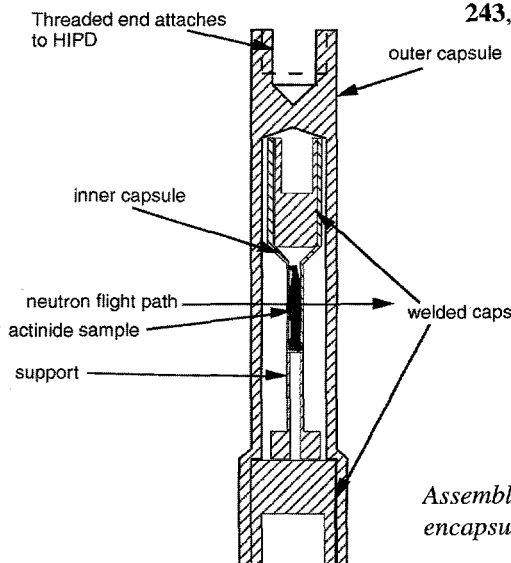
Structural and Magnetic Characterization of Actinide Materials

Barbara Cort

The focus of this project is to extend our fundamental research capability and to answer questions of practical importance to stockpile integrity and long-term storage of nuclear material. We have successfully used neutron scattering techniques to investigate physicochemical properties of elements, compounds, and alloys of the light actinides for the last ten years. We now address new issues vital to the Laboratory's mission such as long-term storage of nuclear materials and aging of plutonium in primaries in the nuclear stockpile.

We made significant progress in development of encapsulation techniques for milligram quantities of actinides for neutron scattering studies. These techniques are important for studies of rare isotopes available only in small quantities or isotopes that are difficult to handle in larger quantities because of their radiological properties. We performed a successful test on a nonradioactive sample using the encapsulation assembly shown in the first figure. We

observed clear diffraction peaks, as shown in the second figure, for 15 mg of CaF_2 counting for two hours on the Manuel Lujan Jr. Neutron Scattering Center's high-intensity powder diffractometer (HIPD). We used these results to calculate patterns for two actinides of interest, AmD_2 and PuO_2 , each counted for 24 hours (see second figure). We predict well-defined diffraction peaks.

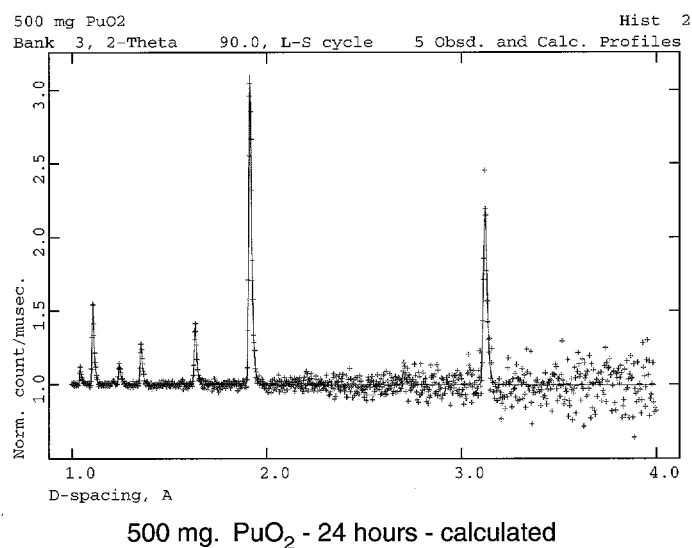
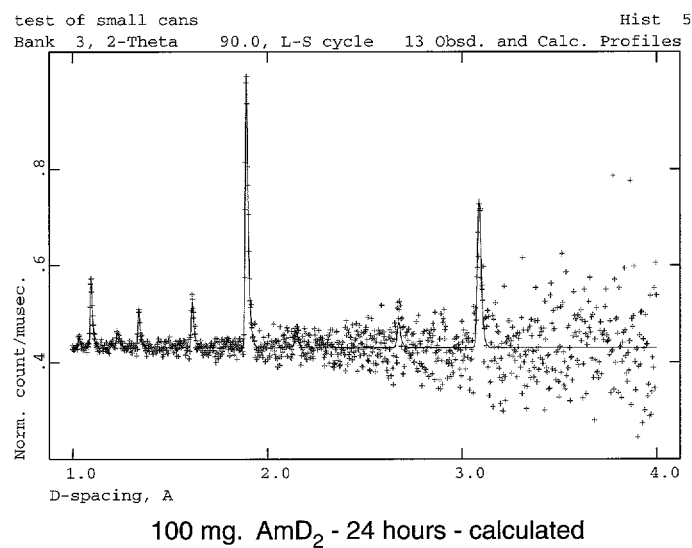
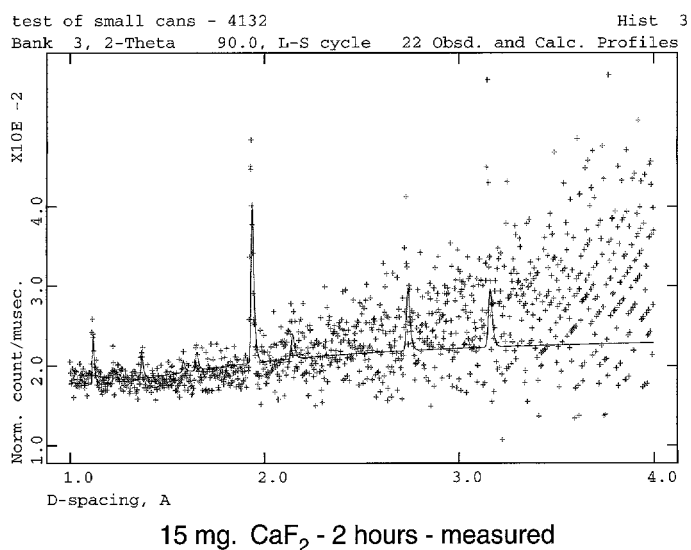


Assembly drawing of the small sample encapsulation; scale is 2:1, in inches.

Based on these results, we plan to use neutron diffraction to investigate the nature of intriguing changes in the temperature dependence of the resistivity of $\text{AmD}_{2.5}$. We will also perform neutron diffraction experiments to determine the structures of superstoichiometric oxides of plutonium produced from the reaction of plutonium oxides with water under storage conditions.

Publications

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Neutron diffraction data for CaF_2 (top) and calculated patterns for AmD_2 and PuO_2 .

Equation-of-State, Thermodynamic, and Structural-Mechanical Properties of Intermetallic Compounds

John Wills

Intermetallic compounds have important applications as high-temperature structural materials. Their elastic, mechanical, and structural properties as a function of temperature, pressure, and composition are key measures of their usefulness. The goal of this project was to develop the theory and resources to perform *ab initio* calculations of (1) the elastic properties of high-temperature structural materials, (2) the structural properties of ordered alloys, and (3) the equation of state of materials.

For our first goal, calculation of the elastic constants of C15 NbCr₂ was completed during this fiscal year, as well as calculations of the relative structural stability of C15, C14, and C36 NbCr₂ and HfV₂. (C14, C15, and C36 designate various crystal structures.) We calculated the isotropic shear modulus from Reuss/Voigt averages and compared them with

experimental data; theory and experiment appear to be in significant disagreement. These calculations were done on the related structural materials NbCr₂ and HfV₂ instead of the originally proposed Ti-Al and Ni-Al systems because of the timely availability of new experimental data with which to compare.

Toward our second goal, we developed and tested a method for performing *ab initio* electronic structure calculations on ordered alloys. This method improves on the virtual crystal approximation for full potential calculations of inter-row alloys. We applied this method to the calculation of structural stability of (Ti, Zr)-(V,Ta) alloys for comparison with experimental results; experimental results are thus far disappointing, and we are applying the method to elasticity in Nb-Cr alloys.

Finally, because of recent developments in *ab initio* calculations of linear response functions, we put aside our third goal of using fitted potentials to generate a full-zone phonon spectrum in favor of the development of the resources to perform *ab initio* calculations of full-zone phonon spectra using linear response theory. We completed the development of the theory of this capability for the electronic structure method that we use. We also tested the calculation of forces for a variety of materials. The capability to calculate phonons with linear response is currently being written into our electronic structure codes.

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Neutron Scattering from Correlated-Electron Systems

Robert Robinson

The purpose of this project is to exploit the neutron scattering facilities at the Los Alamos Neutron Science Center in the studies of correlated-electron behavior in both f-electron systems (e.g., heavy fermions) and transition-metal oxides (like the high-temperature superconducting cuprates). There are two main thrusts: (1) the use of pair-distribution-function (PDF) structural methods to study local disorder, particularly in the cuprates, and (2) the use of inelastic neutron scattering for the study of magnetic excitations in such

systems. The PDF method consists of analyzing the data in real (rather than reciprocal) space, much as one does in measuring pair distribution functions in glasses or liquids; it complements more conventional crystallographic methods like Rietveld refinement. Inelastic neutron scattering is the technique of choice for measuring the magnetic excitation spectra in such systems.

We performed a number of highly successful inelastic scattering studies on the PHAROS high-resolution chopper spectrometer. These included a study of the temperature depen-

dence of the 40-meV crystal-field level in UPdSn, a search for crystal-field excitations in UPd₂Pb, and a definitive experiment on the crystal-field level in PuO₂. The PuO₂ experiment showed, in contrast to a previous lower-resolution experiment at Argonne National Laboratory, that there is no quadrupolar splitting of this level, but that there is some residual broadening.

On the diffraction side, we studied the Li-doped version of La₂CuO₄, the parent compound for the high-temperature superconductors, by means of conventional neutron diffraction. Both the structural and thermal parameters are unusual and indicate that the local and average structures are not identical.

Advanced Deformation Process Modeling

U. Fred Kocks

The general aim of this project was to improve the understanding of the constitutive behavior of metals for use in deformation processing applications. This project has had two major components: the description (on the basis of dislocation mechanisms) of the kinetics of flow and strain hardening and the description (on the basis of polycrystal plasticity models and measured textures) of the anisotropy of macroscopic strength properties. Progress was made on both fronts, with the following highlights.

The overall status of our strain hardening theory was reviewed and compared with some new proposals (which were found wanting). In particular, the processes of dynamic recovery seem well understood, but this knowledge is not always applied to best advantage. Some inroads have been made into improving the general appreciation of this part of plasticity theory.

For a long time, and according to all investigators, the prediction of deformation textures has suffered from yielding textures that are too sharp, compared with experiments. A systematic investigation of the influence of texture sharpness (real or perceived) on macroscopic properties has demonstrated that this effect is negligible in most cases. On the other hand, slight shifts in the location of texture peaks, whether as a result of experimental errors or of faulty model predictions, can have significant effects on strain anisotropies, such as those causing the so-called earing in deep-drawn metal sheets.

Continued cooperation with Armand Beaudoin of Reynolds Metals Corporation and with Heinz Mecking of the Technical University Hamburg-Harburg (Germany) has been very effective, both from the modeling and from the applications point of view.

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Scanning Probe Microscopy Competency Development

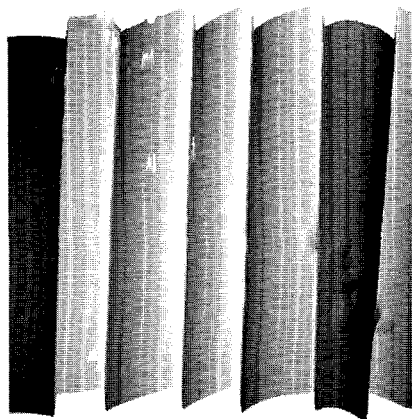
Marilyn Hawley

Our goal is to develop the ultra-high-vacuum (UHV) scanning tunneling microscope system to include in situ film fabrication and complementary analytical capabilities. We plan to integrate this system with existing scanning probe and surface technologies. A broad range of applications will be enhanced from the existence of a range of scanning probe instruments and the associated state-of-the-art expertise, particularly at the nanoscale level. Of particular value is an extension of the present capabilities for examining surfaces in air to include the measurement of surfaces prepared under clean (vacuum) conditions.

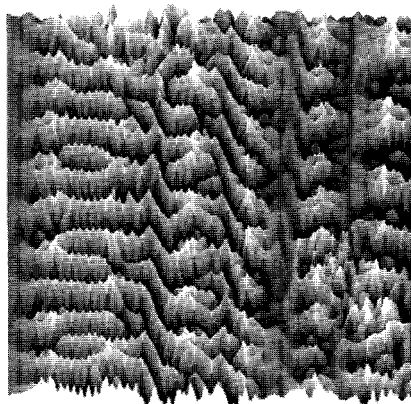
We have now modified the system to include a new vacuum chamber, a new load-lock system for sample insertion, and sample positioning and sample heating capabilities for both

metal and semiconductor materials. In addition, we have added magnetic and electric force capabilities to the air scanning probe and have used these capabilities to perform growth and characterization studies of magneto-resistive films. We have obtained some preliminary data on magnetic structure of thin films and stressed magnetic ribbons, as shown in the accompanying figure.

The combined capabilities now enable us to respond to a wide variety of problems requiring localized imaging of conducting and nonconducting surfaces in liquids, air, UHV, and at low or elevated temperatures. We will further expand these capabilities to include imaging during or after in situ mechanical stressing of materials. Work has begun on adding nanoindenting, scratching, and in situ tensile stress capabilities.



Topograph



Magnetic Image

Tapping-mode atomic force microscope images, shown in profile, of the surface of a stressed Fe-Si-B magnetic melt-spun amorphous ribbon. The left-hand image shows the surface structure of the slip bands, while the right-hand image shows the corresponding magnetic structure due to magnetoelastic effects that can be associated with residual stress in the ribbon. The magnetic image was made possible through the employment of noncontact and field gradient techniques and the use of a CoCr- or permalloy-coated silicon tip. In this technique, the images are collected simultaneously. Topographic and magnetic information is collected during alternate line scans.

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Design and Implementation of an X-Ray Strain Measurement Capability Using a Rotating Anode Machine

Joyce Roberts

Residual stresses close to the surface of materials can improve the reliability and lifetime of parts such as gears, spindles, and axles for technological applications. An exact knowledge of the stresses at the surface and their depth distribution is important. X-ray diffraction plays a significant role in measuring surface residual stresses. Our project is focused on developing an x-ray capability as a key to measuring and interpreting strain effects.

We used finite-element models to predict the thermomechanical processing effects on the residual stresses in a unidirectionally reinforced SCS-6/Ti-6-2-4-2 [0]6 material, and we used x-ray and neutron diffraction to measure the effects. Both x-ray and neutron diffraction recorded a reduction in stresses in the processed material compared with the as-fabricated material. The decrease correlated with improvement in fatigue lifetime.

A novel approach developed at Cornell University employs the volume shrinkage that accompanies reduction reactions to induce compressive residual stresses in the surfaces of ceramics. In this approach, alumina is bonded to a nickel-spinel oxide sample during hot pressing. When the spinel is reduced, it shrinks, inducing compressive residual stresses in the alumina. Our preliminary x-ray measurements indicate that the

residual stresses present in the alumina fall below the predicted values.

Reduction reactions can also be applied to magnetic metal-ceramic thin films. Nickel-spinel is reduced to obtain thin films containing nanoscale nickel. The nickel particles possess interesting magnetic properties, including perpendicular magnetization. Anisotropic residual stresses present in the nickel because of the volume shrinkage and the coefficient of thermal expansion mismatch are believed to be the cause of the perpendicular magnetization. Our preliminary x-ray stress measurements have yielded tensile stresses of several hundred megapascals; these measurements correlate well with magnetic anisotropy data obtained at Cornell.

Another method for measuring stress, the crack-compliance method, offers a unique capability for measuring stress variation with depth. A slot incrementally introduced into a part containing residual stress causes local relaxation. The resulting surface

strains are measured at each increment of slot depth and are used to solve for the original residual stresses. Using this technique, we compared the results of the crack compliance method with x-ray and neutron diffraction measurements. These comparisons are shown in the accompanying figure.

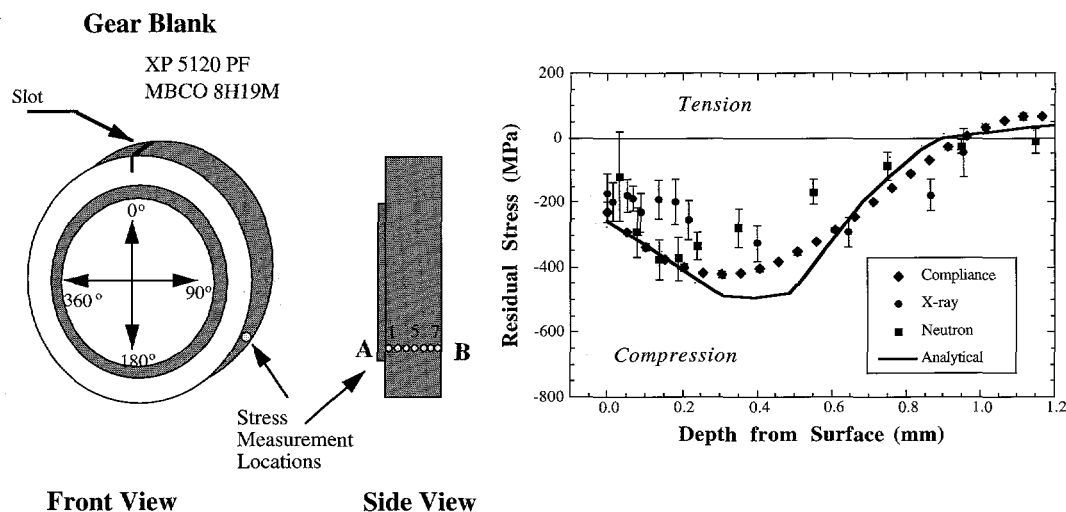
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Comparison of stress measurements on a carburized gear blank (also shown) that were determined using x-ray and neutron diffraction and the crack-compliance method. The results from analysis are also shown for comparison.

Computational Modeling of Materials Processing and Processes

Terry C. Lowe

The objective of this research was to create a computational model to describe the processing of porous, anisotropic materials. The initial focus was on deformation processing of bulk, high-temperature, superconducting oxides. The anisotropic mechanical properties of densified powders composed of Bi-Sr-Ca-Cu-O (BSCCO) are of paramount importance during thermomechanical processing of superconducting tapes and wires. Maximum current transport requires high relative densities and high degrees of alignment of the single-crystal superconducting planes parallel to the plane of the tape. This configuration causes high stresses during compressive processing modes and can lead to cracking and thus degrade the density and conductive properties of the tape.

Early in the project we developed a model to describe the mechanical behavior of BSCCO during deformation processing. The model combines theories of deformation for porous, elastic-viscoplastic, polycrystal materials. We conducted compaction experiments on 2223 BSCCO powder in a confined channel-die environment to obtain data for calibrating the model. We then compared the model with other experimental results and used them to resolve the effects of initial texture and confinement pressure on the densification and ultimate formability of the BSCCO powder.

We performed a detailed, finite-element analysis of the tape-rolling environment and calculated both pressures and shear strains in the core of oxide powder-in-tube (OPIT) processed tapes. In addition, we

investigated rod-in-tube processing and rolling with extra packing material. The calculated deformations were then applied as boundary conditions to the model we developed. We used the calculated results to interpret a set of prototypical rolling experiments designed to investigate core morphologies resulting from various rolling environments. Our goal was to understand the deformations in the core of the OPIT workpiece and the resulting microstructural evolution of the BSCCO powder. We were able to simulate the effects of multiple processing parameters on the texture and density of the superconducting material. One of the most significant results was the prediction of the important role of shear deformation on the evolution of textural anisotropy.

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Nanometer-Scale Materials

David Devlin

Our focus is the science and technology needed for molecular-level control of materials on a nanometer scale—from advanced computing architectures to microelectronics and catalysis. Molecular-level control that relies on artificial structures and nanometer-scale materials will help us develop entirely new devices and chemistries.

Using the metal amide $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$ as a molecular precursor, we prepared highly selective, alumina-supported, molybdenum carbonitrides by solution impregnation. On the basis of relative weight percents, these materials demonstrate a 5- to 8-fold increase in catalytic activity over similar materials prepared by traditional, solid-state approaches.

The catalytic activities of these materials depend on the type of

alumina support used. Impregnation of $\text{Mo}_m\text{C}_x\text{N}_y$ into preformed alumina pellets resulted in a material that specifically isomerized n-heptane into equal amounts of 2- and 3-methylhexanes and iso-butane. We saw no evidence of aromatic products at operating temperatures below 420°C. The product selectivity of the isomers was 56% at an n-heptane conversion efficiency of 57%. Impregnation of $\text{Mo}_m\text{C}_x\text{N}_y$ into an alumina powder resulted in an extremely selective aromatization and dehydrogenation material. The products from this material consist only of aromatics and n-heptenes with less than 2% isomerization or cracking products.

We developed scanning force microscopies (atomic force and lateral force) to probe the microscopic

structures of self-assembled, monolayer systems (SAMs). Lateral force microscopy proved especially useful in imaging patterned SAMs formed using microcontact printing techniques. We were surprised to observe differences between SAMs of alkanethiols on gold in stamped versus filled-in regions of u-contact, even when the molecules were identical. We studied these patterned SAMs, using Fourier transform infrared and other spectroscopic methods, and now attribute the difference between stamped and filled-in areas to density differences in the SAMs.

Publications

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Science and Technology of Reduced-Dimensional Magnetic Materials

Robert Heffner

Our research objective is to develop a clear microscopic understanding of the physical mechanisms responsible for the unusual electronic transport properties exhibited by the transition-metal oxides $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ (where M can be calcium, barium, or strontium). These materials typically undergo a very large reduction in resistance in modest magnetic fields near their ferromagnetic transition temperatures, making them strong candidates for important technological applications. Our efforts combine the three key tools of advanced materials research: (1) materials synthesis (single-crystal and polycrystal growth techniques); (2) physical characterization (x-ray diffraction, electronic transport, magnetization, thermopower, thermal expansion, and magnetostriction); and (3) theoretical modeling.

We have grown large single crystals (7 mm in diameter and 1 to 2 cm long) of the ferromagnet $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ (where M can be calcium or strontium) at the Los Alamos single-crystal facility in the Materials Science Laboratory. Thermopower measurements on materials where M is calcium and $x = 0.0\text{--}0.45$ indicate that conventional transport models with nominal valence cannot account for the small (doping-independent) magnitude of the high-temperature-carrier contribution to the Seebeck coefficient. Because the number of active carrier sites is less than expected from the doping x ($x = \text{Mn}^{3+}$ concentration), charge disproportionation (2Mn^{3+} goes to $\text{Mn}^{2+} + \text{Mn}^{4+}$) may be important in these systems.

In the theoretical realm, we have carefully analyzed the double-exchange model and found that the ground state and the low-lying magnetic excitations are far richer than often assumed in approximate and mean-field treatments. This result

is consistent with a variety of experimental data (e.g., neutron pair-distribution function analysis, x-ray absorption fine-structure analysis, thermopower) and with the fact that real materials involve orbital interactions, disorder, and Jahn-Teller electron-lattice coupling.

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Complementary Neutron Diffraction and Computational Micromechanics Studies of Polycrystalline Deformation in Advanced Materials

Mark A. M. Bourke

The objectives of our project are to use neutron diffraction to improve the understanding of polycrystal deformation and to relate the results to micromechanical models. The scope includes measuring residual and in situ loading strains, as well as thermal relaxation effects. We have selected several materials for study and, to date, have performed measurements on NiAl-AlN-Al₂O₃ composites, CuMo, austenitic steel, and NiTi composites.

Our effort in computational modeling has focused on validating a self-consistent elastic-plastic model used to predict the response of a face-centered cubic stainless steel. The model predicts elastic lattice strains (that develop within subsets of grains in predetermined orientations) which are then compared with the measured values

averaged over the bulk using neutron diffraction. To date, we have observed good agreement between the predicted and measured values for strains parallel to the load, whereas we found significant differences between the two values for strains perpendicular to the load.

In developing the experimental capabilities, we purchased a 1200°C controlled-atmosphere furnace and adapted it for operation on the neutron powder diffractometer at the Los Alamos Neutron Science Center. During the next year, we will use this furnace to determine relaxation temperatures of NiAl-based composites. In a separate development, we implemented two infrared lamp heaters on an existing stress rig and are presently performing creep studies on a model CuMo system.

Characterization of Active Sites in Zeolite Catalysts

Juergen Eckert

Atomic- or molecular-level details of the interaction of adsorbed molecules with active sites in catalysts are urgently needed to facilitate development of more effective and/or environmentally benign catalysts. To this end we are carrying out inelastic neutron scattering (INS) studies combined with theoretical calculations of the dynamics of small molecules inside the cavities of zeolite catalysts.

Our principal approach has been to utilize molecular hydrogen (H_2) as a probe of active sites in the zeolite. The interaction of H_2 with adsorption sites gives rise to a barrier to rotation for the molecule, which is readily obtained by INS techniques. We found that this barrier differed substantially for different sites.

The unit cell of zeolite A is shown in the accompanying figure. Each vertex is occupied by either a silicon or an aluminum atom, and these vertices are bonded to one another via an oxygen atom. Cations, such as Na^+ , are located on extraframework sites. Three of these cations are shown: Na I approximately in the plane of a six-ring (a ring of six vertices), Na II in the plane of the large eight-ring (the opening to the large cavity called the supercage), and Na III above the four-ring. With the aid of Quantum Monte Carlo simulations, we were able to show that an area near the four-ring is the most likely adsorption site for H_2 in zeolite A, and we established a trend for adsorption near a variety of divalent cations (located near the six-rings) exchanged for Na^+ . Coadsorption of N_2 and H_2 displaced H_2 from

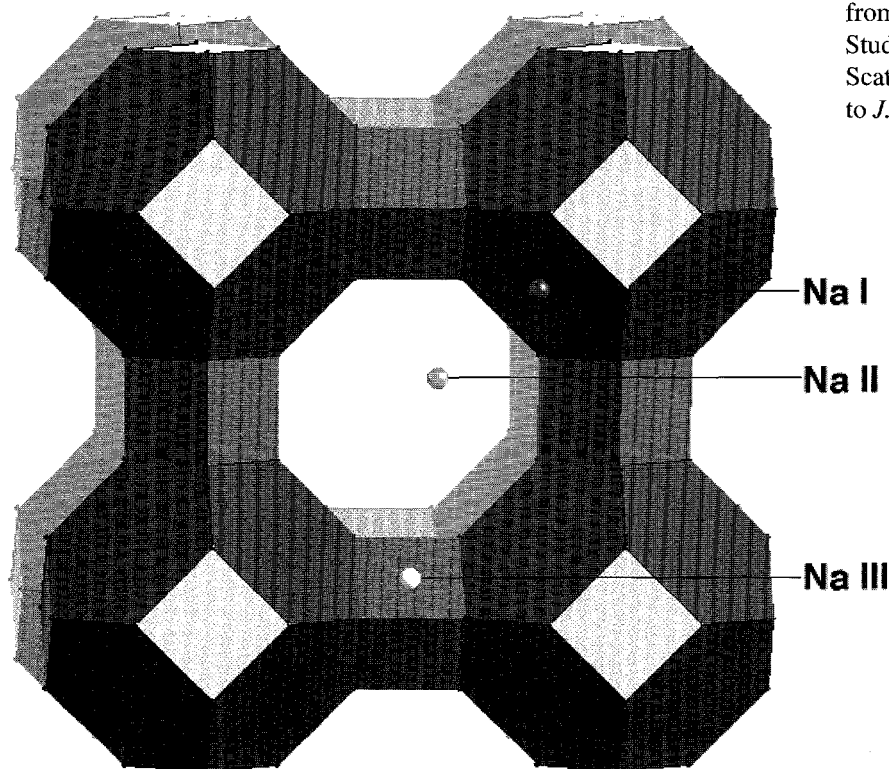
the preferred adsorption sites and enabled us to identify secondary adsorption sites.

Our INS studies of the adsorption of other small molecules (water, ethylene, and cyclopropane) serve as a benchmark for theoretical calculations of the dynamics of adsorbates in catalysts. We experimentally determined the modes of adsorbed ethylene in zeolite NaX and found these modes to be in excellent agreement with the results of *ab initio* calculations. We also demonstrated the utility of INS spectroscopy to monitor slow reactions in zeolites by observing isomerization of cyclopropane in partially Cu^{2+} -exchanged zeolite A.

Publications

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Unit cell of zeolite A with three cationic sites. Adsorption of H_2 is strongest near Na III.

New Initiatives in Materials Characterization, Modeling, and Synthesis

Don Parkin

This project is a collaboration between Laboratory and external materials science researchers to explore new techniques in a variety of areas related to the characterization, constitutive modeling, and synthesis of materials. Specifically, in the area of characterization, the focus is on expanding strengths in electron, scanning-probe, and atomic force microscopy and x-ray and neutron characterization of matter, and to do this in collaboration with outside academic institutions. In modeling, the focus is on improving our ability to model both the fundamental electronic structure of materials and their mechanical behavior. Another goal is an improved ability to synthesize different kinds of materials ranging from electronic to structural materials.

As part of the collaboration, we held three major workshops on the following topics to explore the state of the art and potential scientific

advances: "Ion Interactions and Radiation Damage," "Materials Solidification," and "Fundamental Electronic Structure of Plutonium." The radiation damage workshop focused on fundamental aspects of radiation effects on ceramic materials and nuclear material waste forms. The workshop on solidification focused on casting processes, including plutonium casting issues. The electronic structure workshop addressed fundamental issues in modeling the electronic structure of f-electron materials (actinides).

In related activities, we developed an alternative to the standard molecular dynamics approach for atomistic simulation of dislocation crossing, annihilation, and short-range forces. We also developed a high-temperature probe for operation in the National High Magnetic Field Laboratory's 20-T magnet and measured the high-temperature Hall constants.

Publications

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Dynamics of Polymers at Interfaces

Gregory Smith

This project addresses fundamental questions concerning the behavior of polymers at interfaces and poses the following questions: What processes control the formation of an adsorbed layer on a clean surface? Can we accurately predict the structure of nonequilibrium layers? What processes control the desorption or displacement of preadsorbed polymers?

Last year we performed the first experiments to study the nonequilibrium architecture of polymer layers strongly adsorbed from the polymer melt. We constructed a sample holder for our film-spinner that supported the weight of the quartz crystals for the experiment (the crystal dimensions were $1.5 \times 3 \times 0.5$ in.). Hydrogenated

(poly)methyl methacrylate (H-PMMA) was spin-coated onto the quartz crystal surfaces and subsequently annealed at melt conditions. After cooling, unbound material was leached away in a solvent bath.

Using neutron reflection (NR), we investigated the architecture of the residual bound layer swollen in good solvent (benzene) or collapsed against a nonsolvent (D_2O). The quartz crystals were mounted in a specially designed cell, which placed the coated surfaces in contact with a solvent and at the same time permitted the NR studies. We measured the reflectivity of neutrons, $R(q)$ vs q (q is the neutron's momentum transfer) at the Manuel Lujan Jr. Neutron Scattering Center for

both swollen and collapsed layers for several molecular weights. Collapsed layer thicknesses generally increased with molecular weight. Data for swollen layers suggest diffuse segment-density profiles. A detailed analysis will allow us to verify the Guiselin theory of adsorbed polymers, which in turn will allow us to predict the structure of nonequilibrium layers.

In a separate experiment, the residual layer was overcoated with a layer of deuterated PMMA (D-PMMA) and the system annealed at the melt conditions. Subsequent leaching and interrogation by NR indicated substantial replacement of the strongly adsorbed H-PMMA by D-PMMA in the overcoating, suggesting that the residual H-PMMA layers studied were formed by sudden immobilization at the surface of an equilibrated melt. These studies give us clues into the process of displacement of adsorbed polymers.

Understanding and Controlling Self-Assembly

Basil Swanson

The fields of self-assembly and self-organizing mesoscale structures have grown rapidly over the past decade. In addition to fundamental research that spans simple self-assembled monolayers (SAMs) to complex, biologically inspired self-organizing structures, there has been increased interest in applying self-assembly to produce useful, functionalized materials. In order to enhance useful materials properties, we must first understand the relationships between structure and function in SAMs and in more complex self-assembled structures that incorporate specific functional groups (for example, donor-acceptor complexes, molecules with high optical nonlinearity, and reagents for molecular recognition).

The overall objectives of this project are to develop an in-depth understanding of how complex molecular structures form by self-assembly and how the individual molecular components and bulk functionality are interrelated. Our approach is to (1) experimentally characterize and theoretically model intra- and interplanar ordering of model SAMs in an effort to understand and control the self-assembly process, (2) develop new experimental probes of mesoscale structure and use them to augment more traditional characterization methods, (3) prepare well-ordered model SAMs and characterize their mesoscale structures using the experimental probes, and (4) couple theory and experiment to develop models that will allow us to predict mesoscale structures and, thus, to synthesize SAMs with optimal physical properties.

During this year we used scanning force microscopies to image patterned, alkanethiol SAMs that we formed on gold using microcontact printing, and we correlated the results from the imaging with spectroscopic studies. We discovered that the different densities of stamped and solution-grown SAMs of hexadecanethiolate on gold caused the

frictional and compressional force differences that we observed with scanning force microscopies. Using spectroscopic techniques, we probed the structures of different end-functionalized, alkanethiol SAMs and found the results to be consistent with nanoscale cluster formation. We also began studying new techniques (sum-frequency generation and surface-enhanced Raman spectroscopy) for characterizing the organic-inorganic interface.

To simulate the behavior of the SAMs of alkanethiols adsorbed on gold, we wrote a new, large-scale, massively parallel molecular dynamics (MD) code. In addition, we performed *ab initio*, quantum-chemistry calculations of the sulfur-gold potential-energy surface and used these calculations to develop a detailed model of the organic-inorganic (specifically, the sulfur-gold) surface. From this model we developed an empirical function describing the sulfur-gold interaction and used it in MD calculations. We also further developed a three-dimensional analog of alkanethiol SAMs and studied it using a variety of structural and spectroscopic probes.

Publications

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Role of Charge Localization in the Basic High-Temperature Superconductivity Mechanism

P. Chris Hammel

Local structure profoundly affects the superconducting, normal electronic, mechanical (for example, elastic), and other response functions of materials. By emphasizing cuprates, our project examines this difficult, important, and as yet barely studied problem of structure. We have been focusing on oxide superconductors, and related nonsuperconducting compounds, by using an array of experimental and theoretical techniques to characterize the local structure and its correlations, measure the effects of the local structure on superconducting and other macroscopic properties, and create a new theoretical understanding of high-temperature superconductors.

This year, we have used nuclear magnetic resonance to study the doped-hole state in $\text{La}_2\text{Cu}_3\text{Li}_5\text{O}_4$ (LiLCO) and found a surprisingly low-lying excitation. We have used electron, x-ray, and neutron diffraction to investigate the structure of LiLCO and its magnetometry, which will then enable us to characterize the material's magnetic properties. We have found that the temperature and nickel-content dependencies of the thermal conductivity of several nickel-doped bismuth cuprates (BSCCO) between 0.05 and 2 K are contrary to theoretical predictions.

We have developed a self-consistent treatment of magnetic and nonmagnetic impurity states in d-wave superconductors, which result in strongly anisotropic quasi-particle states; formulated a three-dimensional model for layered superconductors that couples structural buckling and strong electron-electron interactions in the a-b plane to antiferroelectric polarizability fluctuations in the

c-direction; begun a systematic study of spin-charge-lattice coupling in Peierls-Hubbard models in the context of charge (polaron) ordering in LiLCO and in the context of striped superlattice phases in hole-doped CuO_2 planes; understood the broken-symmetry solutions observed in *ab initio* cluster calculations on the Cu_2O_{11} dimer in terms of an occupation-dependent hopping integral and showed that this rehybridization produces an attractive interaction; and proposed a strong coupling explanation for why pairing should have d-wave symmetry in the presence of antiferromagnetic correlations.

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Measurement by Neutron Diffraction of Strains in Advanced Engineering Structural Materials including AlSiC and AlTiC

Mark A. M. Bourke, Los Alamos National Laboratory
David C. Dunand, Massachusetts Institute of Technology

Drawing on our earlier work with AlTiC and given the similarity in mechanical properties, we chose to examine a shape-memory alloy composite (NiTiTiC). Initially we concentrated on the composite's matrix (NiTi). Using neutron diffraction, we studied the formation of stress-induced martensite in superelastic NiTi during uniaxial compressive loading and unloading. Using a Rietveld refinement with a March-Dollase texture formulation, we determined the martensitic and austenitic phase fractions as a function of the applied stress. Before loading, the specimen was fully austenitic. At the highest applied stress (-625 MPa), about 90% of the austenitic phase had transformed to martensite, with a concomitant macroscopic strain of -2.8% . Upon unloading, all of the stress-induced martensite reverted to austenite, and the totality of the macroscopic strain was recovered. We determined the propensity for various austenitic crystallographic orientations to transform at different stresses.

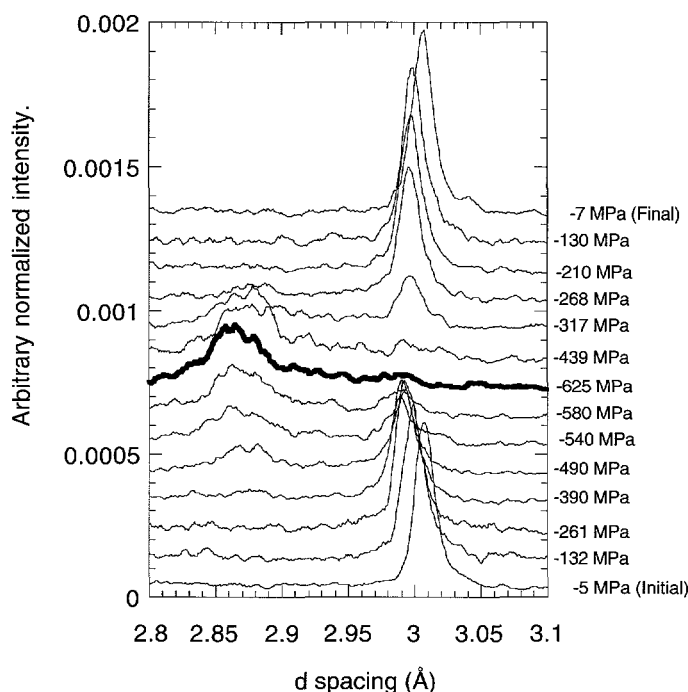
After yield at a stress of about -350 MPa, plastic deformation resulted from the austenite-to-martensite transformation. The difference in structure between the unstressed and stressed states was visible in the broad martensitic peaks that were clearly discernible from the sharp austenite peaks. The progression and reversibility of the transformation are illustrated in the first figure, which shows a short section of the spectra for each stress level. Upon loading, the shift to shorter d-spacings

resulted from increasing elastic compressive strains, while the decrease in intensity of the austenitic peak and simultaneous increase in the martensitic peak were due to transformation. The stress-dependence of the phase volume fractions determined by these refinements are shown in the second figure. One unexpected result was that about 90% of the austenite was transformed to martensite at a macroscopic strain of only -2.8% .

Publications

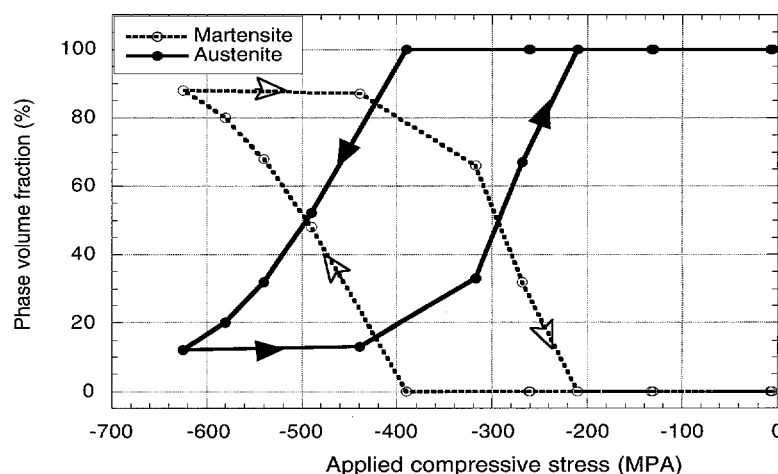
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Displaced spectra showing a short section of the diffraction patterns obtained with the scattering vector parallel to the loading direction. The austenitic $[100]$ at 3.0 Å reduces in intensity to 0 at -625 MPa. Conversely the martensitic $[100]$ at 2.86 Å becomes visible at -490 MPa and reaches a maximum in intensity at -625 MPa (bold line). The shift to shorter d-spacings is due to the increasing elastic compressive strain. The data has been smoothed and displaced vertically for clarity.

The relative intensities of the austenitic and martensitic diffraction patterns can be converted to volume fractions of the two phases. Martensite starts to form at compressive loads greater than -400 MPa; upon unloading, however, it remains present until below -280 MPa.



Chemistry and Microstructure of High-Temperature Superconductor Interfaces

Quanxi Jia

The research objectives of this project are to investigate the interface chemistry, physics, and microstructure of superconductor and normal-metal composites and to use these composites to develop high-performance superconducting quantum interference devices (SQUIDs) with controllable and reproducible properties. SQUIDs are state-of-the-art ultrasensitive devices that detect very low magnetic fields. Among other applications, they are used to nondestructively evaluate materials, measure the biomagnetism of human living organs, measure gravity in mineral surveying, and detect underground bunkers and submarine communication.

At the core of this project, we are developing composites and investigating the mechanisms that control the electrical properties of the materials. This year, through processing control and material engineering, we investigated the interface chemistry and microstructure between superconductor and normal-metal layers of the devices. We fabricated superconducting Josephson junctions (two superconductor electrodes separated by a thin barrier, across which current flows without a voltage drop) and dc

SQUIDs using an edge-geometry superconductor/normal-metal/superconductor (SNS) configuration. We used Ag-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as electrodes and $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$ as the normal-metal barrier. The $I_c R_n$ value (the product of the critical current and the junction resistance) was in the range of $120\text{--}140\ \mu\text{V}$; we determined this value from the current-vs-voltage characteristic of the devices. The dc SQUIDs showed a differential-flux modulation depth, $dV/d\Phi$ (where V is voltage and Φ is flux), of greater than $150\ \mu\text{V}/\Phi_0$ at $75\ \text{K}$ ($\Phi_0 = 2.07 \times 10^{-15}\ \text{Wb}$). More than 90% of the SQUIDs on a chip (14 dc SQUIDs on a 1-cm^2 LaAlO_3 substrate) showed well-behaved voltage-vs-flux characteristics. Three typical measures of performance are the SQUID modulation depth, the SQUID noise, and the process control. We obtained devices at $75\ \text{K}$ with a modulation depth of $49\ \mu\text{V}$, a noise value of $5\ \mu\Phi_0/\text{Hz}^{0.5}$ at $1\ \text{kHz}$, and a standard deviation in SQUID resistance of 11%. All these values are superior to the best results for SNS-configured device structures from other research groups.

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Texture Science and Technology

Michael Stevens

The objectives of this project are to (1) perform basic research on the effects of texture on material properties, (2) increase the utilization of texture and anisotropy information through texture analysis, and (3) improve our texture measurement and modeling capabilities. Texture refers to studying the orientation, shape, and size of the individual crystals in polycrystalline materials.

We have made significant progress on advanced texture analysis algorithms that use many pole figures (diffraction peaks) and a few sample orientations. Our new algorithm greatly reduces the data collection time needed at a time-of-flight neutron diffraction facility. It combines crystallographic Rietveld analysis of diffraction spectra with calculations of orientation distribution functions. The algorithm is particularly useful for monochromatic

radiation with position-sensitive detectors or for polychromatic radiation. Full diffraction spectra may now be used in the analysis, resulting in maximum use of data. We applied our advanced texture algorithm to a sample of experimentally deformed limestone and produced excellent simultaneous results on the sample's texture, crystal structure, microstructure, and residual stress. It appears that the algorithm's methodology is applicable to low-symmetry and polyphase materials with complicated diffraction spectra; such materials presently elude quantitative texture analysis.

Through our collaboration with the Geology Department at the University of California, Berkeley, we refined our BEARTEX software to allow simultaneous goniometer control and data acquisition on both of our x-ray texture diffractometers. The improvements allow operation with a common

WINDOWS desk-top computer and better coverage of orientation space.

After comprehensively reviewing orientation-imaging microscopes and data collection and analysis hardware and software, we ordered a Philips field-emission-gun scanning electron microscope (SEM). This SEM will allow us to map orientations on a subgrain scale and determine misorientations between grains in polycrystalline aggregates. Misorientation data are essential for understanding the process of recrystallization, which is of interest in a variety of structural materials.

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Microstructures of Transition Metal Oxides Characterized by Neutron and X-Ray Scattering

Michael Fitzsimmons

The La-Mn perovskites of the type $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ (where M can be calcium, strontium, or barium, and x varies from 0 to 0.5) are materials which become ferromagnetic at low temperatures. The transition temperature, magnetoresistance, and atomic and magnetic structures of the materials are believed to be determined in part by the valence of manganese, which can be changed through the doping of the M species. Our studies of these materials are concerned with using x-ray and neutron scattering to characterize the

atomic and magnetic structures and vibrational modes of the perovskites.

During the past year, we measured the neutron diffraction patterns of two sintered polycrystalline LaMnO_3 samples. The samples were doped with 20 and 33 at. % calcium. The most interesting and challenging experiment involved measuring the effect of a 1-T magnetic field on the atomic structure of the sample doped with 33 at. % calcium. We took the measurements with field on and off and at a variety of temperatures

within two degrees of the transition temperature of the sample. Our analysis of the data is not yet complete. However, we can report that startling changes in the atomic structures of the samples were not observed at any time.

We also examined the atomic structure of a single crystal of LaMnO_3 doped with 20 at. % calcium. We found the structure of this material to be monoclinic with monoclinic symmetry. This result is very surprising in light of the fact that earlier studies of polycrystalline samples, including ours, suggested that the structure of this perovskite was orthorhombic with orthorhombic symmetry.

A Thermodynamically Consistent, Damage-Dependent, Interface Debonding Model for Composites

Bradford E. Clements

The ability to design composite materials and analyze processing procedures relies on the availability of constitutive models that describe the composites' dynamic response accurately. The strength, damage evolution, and failure of interfaces within composites often dominate their macroscopic performance but are not well characterized. The design of such composites for particular applications requires adequate knowledge of interfacial characteristics. Given the large number of potential loading scenarios that an engineering composite can be subjected to, it is extremely beneficial to have reliable and accurate theoretical methods for their quantitative treatment in numerical calculation.

We have developed a method for analyzing interfacial debonding based on the highly successful method of cells (MOC) homogenization technique for composite structures. When perfect interfacial bonding applies, displacement and traction continuity are conditions that are enforced by the MOC analysis. On the other hand, for imperfect interfacial bonding, the displacement becomes discontinuous at the interface. Imperfect bonding is modeled by an interfacial constitutive equation (ICE).

Our specific accomplishments in the past year include quantifying the ICE model for tensile and shear loading in plastic bonded explosives. Furthermore, we have used slightly different ICE formulations to model brittle and ductile interfaces. We have

also implemented the imperfect-bonding MOC model into our three-dimensional finite-difference codes. These models are sufficiently general to allow for laminated systems, long-fiber-reinforced composites, and particulate (discontinuous reinforcement) composite systems. Furthermore, the constituents of the composites are not restricted to elastic crystalline or amorphous solids; the composites can also have viscoelastic properties (i.e., polymeric materials).

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Zircon as a Host Phase for Plutonium Disposition

John Huang

To address problems involving the minimization and long-term storage of nuclear waste, we have proposed zircon (ZrSiO_4) as a host medium for plutonium and other actinides recovered from dismantled nuclear weapons. The objective of this project is to investigate the feasibility of large-scale fabrication of plutonium-bearing zircon. Because PuO_2 is thermodynamically less stable than ZrO_2 , process parameters determined for zircon can be safely applied

to plutonium-zircon. The emphasis of our work, therefore, has been to develop processing parameters that alleviate potential problems in containing nuclear materials during processing.

We have subjected stoichiometric mixtures of ZrO_2 and SiO_2 , in 100-g batches, to hot isostatic pressing at temperatures near 1500°C and pressures of 10,000 psi. Analysis of the product materials by x-ray powder diffraction has shown that after

approximately two hours of reaction time, the materials consist of zircon, although the reaction is not completed. Therefore, fabricating large quantities of plutonium-zircon is feasible. The most significant result of our work is the evidence that container problems exist, which in turn has suggested potential solutions to these problems. Experiments with a quartz inner container, a glass sealant, and a secondary metal outer container are under way in order to find ways of confining contamination during processing.

Many-Body Theory Research

Alexander Balatsky

The foundations of the theory of metals and superconductors have been shaken by a number of discoveries over the last 15 years, including high-temperature superconductors, organic superconductors, and fullerenes. New classes of materials, such as colossal magnetoresistive materials, cuprates, and organic polymers, have a number of properties that favor a much richer spectrum of ground and excited states. These properties include strong electronic and lattice correlations, reduced dimensionality, restricted geometry, disorder, and nonlinearity. The interplay of different effects and the complexity of these materials make the materials suitable for electronic applications.

In this project we are taking on one of the biggest challenges in condensed-matter theory today: we are attempting to understand the behavior of these materials by developing microscopic theories to describe them. This year we focused on heavy-electron physics, including properties of plutonium, and we are working closely with collaborators at a number of universities. One of our collaborators is developing a new model of volume collapse in alpha-delta phase plutonium. This model takes into account the electron-phonon interaction as well as f-d hybridization. Another research group is investigating the charge ordering in Cu-O ladder materials; they found that domain walls tend to form in these Cu-O systems. They also carried out numerical calculations of the optical properties of the two-leg t-J ladder.

A third collaborator has developed the theory that the spin gap in cuprates results from the precursor pairing in cuprates. Other collaborators investigated the role of lithium impurities in La_2CuO_4 and found a novel insulating phase (at 50% lithium doping) with a spin gap of approximately 1500 K. Work on the transport properties of Kondo insulators continues as well.

Another researcher is working on both electronic-structure and many-body computational schemes that have yielded insight into how magnetic states are formed in quasi-one-dimensional systems.

All these described developments are related to the core of our project: a self-consistent treatment of the magnetic and nonmagnetic impurity states in d-wave superconductors. We developed this self-consistent treatment and found that the impurity states have a strongly anisotropic nature.

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Alloy Design and Phase Stability of the Ternary Alloy Ti-Al-Nb

Robert Albers

Several classes of binary intermetallic compounds, such as Ti-Al, have important potential application as high-temperature structural materials because of their high melting temperature, low density, and high strength. The use of these binary alloys is limited, however, by their poor low-temperature ductility and fracture toughness. Adding a third element (e.g., niobium) to these binary alloys is one possibility for improving their low-temperature properties without sacrificing, for example, the desirable high-temperature ductility.

We are using high-precision electronic-structure calculations and molecular dynamics simulations to study the electronic and structural properties of selected ternary intermetallic alloy systems. The goal of our research is to understand and predict the structural stability of these ternary

intermetallics and to understand the correlation between the changes in electronic properties and the improved low-temperature properties in these materials.

During the past year, we focused on the effects of alloying on the energetics of the continuous structural pathway that links the body-centered cubic phase of Ti-Al with the omega phase. Omega phase precipitates modify the mechanical properties of the quenched martensitic alloys by acting as a strengthening element. Our calculations show that under constant volume, pure Ti-Al has an energy barrier to this phase transition. In contrast, our calculations also show that the addition of niobium (substituted on one of the aluminum sites) removes this barrier. The calculations show that the niobium alloy has a clearly different density of states than the pure Ti-Al alloy.

Moreover, the stability of the omega phase (and the presence or absence of an energy barrier) seems to track with d-electron occupation. We are very close to finishing some additional calculations that should show whether these differences can be correlated and explained by directional d-bonding forces due to the extra niobium d-electrons.

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Synthesis and Characterization of Correlated-Electron Materials

Joe D. Thompson

With discoveries—heavy fermions, conducting polymers, fullerenes, and colossal magnetoresistive materials—beyond traditional solid-state physics, we are at the beginning of a golden age for complex electronic materials. These new materials are characterized by strong electronic correlations that arise from competitions between microscopic electronic, magnetic, and structural degrees of freedom. Tuning these competitions by performing chemical substitutions and by varying the pressure, magnetic field, and temperature ultimately controls macroscopic functionalities that will enable next-generation technologies ranging from magnetic sensors and thermoelectric coolers to plutonium applications.

Our objective is to understand and control the coupling and competition among spin, charge, and lattice degrees of freedom in these correlated-electron materials through coordinated efforts in synthesis, characterization, and modeling. Our research focuses on understanding (1) the role of electron-electron and electron-lattice interactions in producing metal-insulator/magnetic-nonmagnetic transitions in transition-metal perovskites (compounds with a cubic structure and chemical form ABO_3), (2) the consequences of mesoscale structure on spin-charge-lattice coupling, and (3) the origin of non-Fermi-liquid behavior in f-electron materials.

We used pair-distribution-function and Debye-Waller analyses of neutron diffraction data to discover evidence for polaron formation (mesoscale structure) and Jahn-Teller distortions in manganite perovskites. We established that the polaron-binding energy reflects strong coupling between lattice and spin degrees of freedom, and we discovered that a volume change is required for a metal-insulator transition in these materials. In addition, we showed that the spin dynamics and electronic structure are unusual for a ferromagnetic metal, and we tested prevailing theories (multi-channel Kondo, proximity to a $T = 0$ phase transition, and disordered Kondo lattice) for the origin of non-Fermi-liquid behavior in f-electron materials with extensive measurements on cerium-, praseodymium-, and uranium-based correlated-electron systems. This experimental effort was closely coordinated with a companion theoretical project, "Theory and Modeling of Correlated-Electron Materials."

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Tailoring the Interfacial Electronic Structure of Organic Electronic Materials and Devices

Ian Campbell

In this project, we are using self-assembled molecular coupling layers to tailor the electronic structure of metal/organic interfaces and organic/organic heterojunctions in order to control the electrical transport properties of these interfaces. Metal/organic interfaces are the essential active element in every organic electronic device, and organic/organic heterojunctions are the key element in efficient, organic light-emitting diodes. Because of their processing advantages, the tunability of their electronic properties, and their flexibility in both materials and device design, organic electronic materials and devices are poised to revolutionize such technological areas as information display and optical communication. Learning to manipulate the electrical transport properties of these interfaces is the key to realizing the potential of organic electronics.

This past year, we used self-assembly techniques to insert a controlled and characterized molecular coupling layer at metal/polymer interfaces. Molecular coupling layers with electric dipoles have been used to manipulate the Schottky energy barrier at these interfaces. We used internal photoemission and electroabsorption techniques to determine these Schottky energy barriers and also to measure basic excitation energies in conjugated polymers. We also developed a theoretical model that describes the current-voltage characteristics of polymer light-emitting diodes.

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Controlling Function of Polar Organic Multilayers

Duncan McBranch

Charge separation on a molecular scale, combined with the large polarizabilities of organic molecules, can be used to design novel, nonlinear optical materials with greatly enhanced performance. Our project involves research in two areas: (1) the design and measurement of new molecular systems that exhibit charge separation and transfer following photoexcitation and (2) the design of approaches for synthesizing multilayers for solid-state electron-transfer devices.

Our strategy for synthesizing multilayers involves self-assembly using alternating positively and negatively charged layers held together by multiple ionic bonds. We have recently synthesized 100 bilayers of nickel phthalocyanine with poly(diallyldimethylammonium chloride). This technique can be generalized to other interesting photosynthetic systems such as conducting polymers. When these conducting polymers (donors) are mixed in blends with fullerenes or other polymers (acceptors), electrons undergo charge transfer in less than 300 fs. We have recently shown that this photo-induced charge transfer provides a recording mechanism for ultrafast photochromic gratings and allows the tailoring of the decay dynamics of recorded holographic gratings. This type of composite charge-

transfer blend constitutes an entirely new class of nonlinear optical material.

A closely related problem involves the design of biomimetic light-harvesting systems that use either photo-induced charge or energy transfer. We have studied model systems that incorporate covalently linked porphyrins to mimic natural photosynthetic pigments. Our results demonstrate the feasibility of designing biomimetic energy-transfer pigments to produce efficient energy transfer with controlled rates. Furthermore, high transfer efficiency can be realized without extensive perturbation of the photophysical properties of the individual "building blocks."

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Pinning Vortices and Enhancing High-Temperature Superconductor (HTS) Critical Currents

Martin Maley

We are investigating flux-pinning mechanisms in high-temperature superconductors to discover means of enhancing HTS critical current density (J_c)—a key performance parameter for superconducting materials. We have achieved large enhancements in J_c at 75 K in barium-strontium-calcium-copper oxide/silver (BSCCO/Ag) conductors by introducing columnar defects, using fission tracks induced by high-energy protons. We have worked to determine the optimum density of columnar defects to maximize J_c and to gain understanding of the mechanisms.

We also carried out two successful studies: enhancing J_c through lower-energy-proton irradiation (500 MeV) and irradiating stacked conductors. We were particularly interested in the commercial feasibility of these processes. We discovered that, at high doses, the intergrain connections are broken, but we found an annealing procedure that heals grain-boundary damage while retaining the enhanced pinning.

The new yttrium-barium-copper oxide (YBCO) conductors prepared by the ion-beam-assisted deposition process contain strong pinning defects of unknown origin that allow them to maintain high J_c at 75 K in high fields. We determined the defects responsible and introduced additional columnar defects by heavy-ion irradiation to seek further enhancements. Patterned bridges in these films show a strong dependence of J_c on the orientation between current and the twin structure. This and other evidence demonstrate that twin boundaries play a major role in the flux pinning. Heavy-ion irradiation produced further substantial enhancements when the magnetic field was aligned with the defects.

Our theoretical investigations discovered a new collective "plasma resonance" mode in layered HTS conductors that is a measure of J_c normal to the superconducting layers.

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Nonlinearity in Structural and Electronic Materials

Alan Bishop

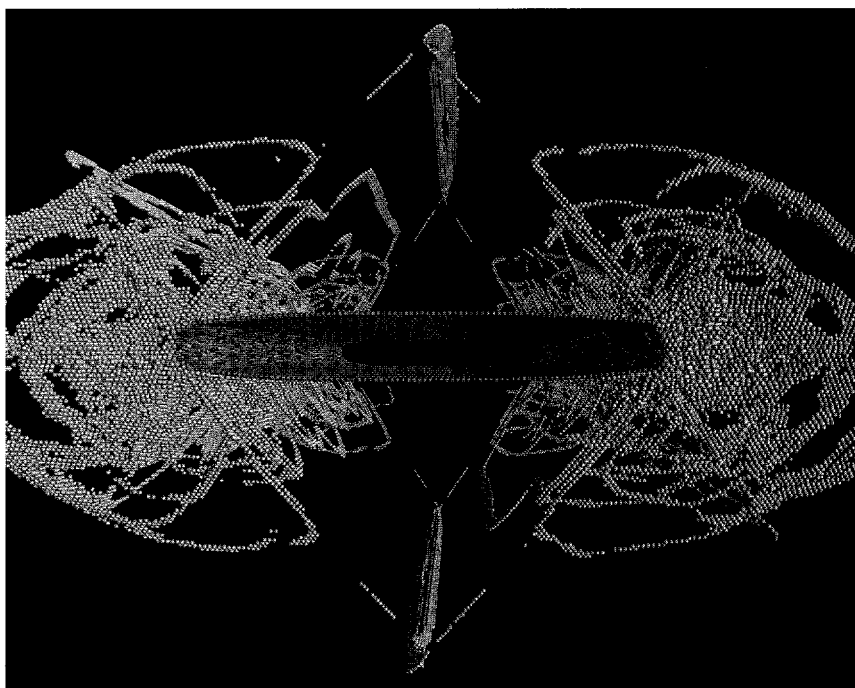
This project has developed and applied a technology base of nonlinear techniques that are relevant to a variety of nonlinear, nonequilibrium problems in condensed matter and materials science. Our controlled synthesis of, and experiments on, novel electronic and structural materials help motivate nonlinear science at Los Alamos, which in turn advances our understanding of the processes that govern the structure and dynamics of today's complex materials. Important concepts from nonlinear science include (1) the prevalence of coherent space-time structures in strongly nonlinear classical and quantum systems, (2) the possibility of deterministic chaos even in low-dimensional dynamical systems, and (3) the coexistence of both coherence and chaos, leading to a rich variety of phenomena connoted by the term *complexity*. Our project studies these concepts and applies them to significant problems in condensed-matter physics and materials science.

Achievements this year include the following:

- large-scale simulations and microscopic modeling of nonlinear, coherent energy storage at the crack tips and sliding interfaces of lattice models (see figure);
- large-scale simulation and microscopic elasticity theory for precursor microstructure and dynamics at solid-solid diffusionless phase transformations;
- large-scale simulation of self-assembling, organic thin films on inorganic substrates;
- analysis and simulation of the smoothing of rough atomic surfaces; and
- modeling and analysis of flux-pattern formation in equilibrium and nonequilibrium Josephson

junction arrays and layered superconductors.

In addition to this work and as part of our communication with others in the field, we organized a seminar series on nonlinear materials and three international conferences on "Fracture, Friction, and Deformation," "Nonequilibrium Phase Transitions," and "Landscape Paradigms in Physics and Biology." We also gave several invited talks, including talks at the international conferences on "Synthetic Metals" and on "Quantum Phase Transitions," at the 1996 CECAM Euroconference, and at the 1995 Fall Meeting of the Materials Research Society.



A 35-million-atom simulation of crack blunting by dislocation emission in copper under tensile loading. An elliptical crack (center of figure) in a 0.1-mm-thick copper sheet is placed under tension in the vertical direction. As the crack attempts to propagate horizontally, it emits clouds of dislocations (white dots), some of which collide directly above the crack. Only atoms at the surface of the crack, or within the cores of dislocations, are depicted. The visualization technique used in the simulation suppresses atoms that are not displaced.

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High-Resolution Electron Microscopy of Advanced Materials

Terence Mitchell

Our objective has been to improve the key performance of a full range of spectroscopy instruments and so increase our ability to analyze advanced materials significantly. The instruments include a field-emission scanning electron microscope (FE-SEM), a 100-kV field-emission scanning transmission electron microscope (FE-STEM), a 300-kV field-emission, high-resolution transmission electron microscope (FE-HRTEM), and a 300-kV analytical transmission electron microscope. We are presently adding a new orientation-imaging microscope.

X-ray energy dispersive spectrometers for chemical analysis are available on all four microscopes, and parallel electron energy loss spectrometers (PEELS) are operational on the FE-STEM and FE-HRTEM. The PEELS systems enable evaluation of local atomic bonding as well as chemical composition in nanometer-scale regions. We have successfully demonstrated the FE-HRTEM point-to-point resolution of 1.6 Å. In addition, because of the high brightness and coherency of the FE source, we have been able to push the microscope's resolution to its information limit of 1 Å by computer reconstruction of a focal series of images.

We have used HRTEM to image the atomic structure of defects such as dislocations, grain boundaries, and interfaces in a wide variety of materials from superconductors to structural ceramics. We have used the new HRTEM to image such defects with much greater accuracy at the atomic level, making it possible to compare them with modeling predictions and improve interatomic potentials.

Recent examples of applications include the characterization of defects and interfaces in thin films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ deposited on various substrates and buffer layers, HRTEM analysis of interfaces in various ceramic composites, analysis of the core structures of dislocations produced in ceramics and intermetallics by high-temperature deformation, and analysis of nanolayered materials. Future applications will involve electron holography by the incorporation of a biprism in the column of the FE-HRTEM.

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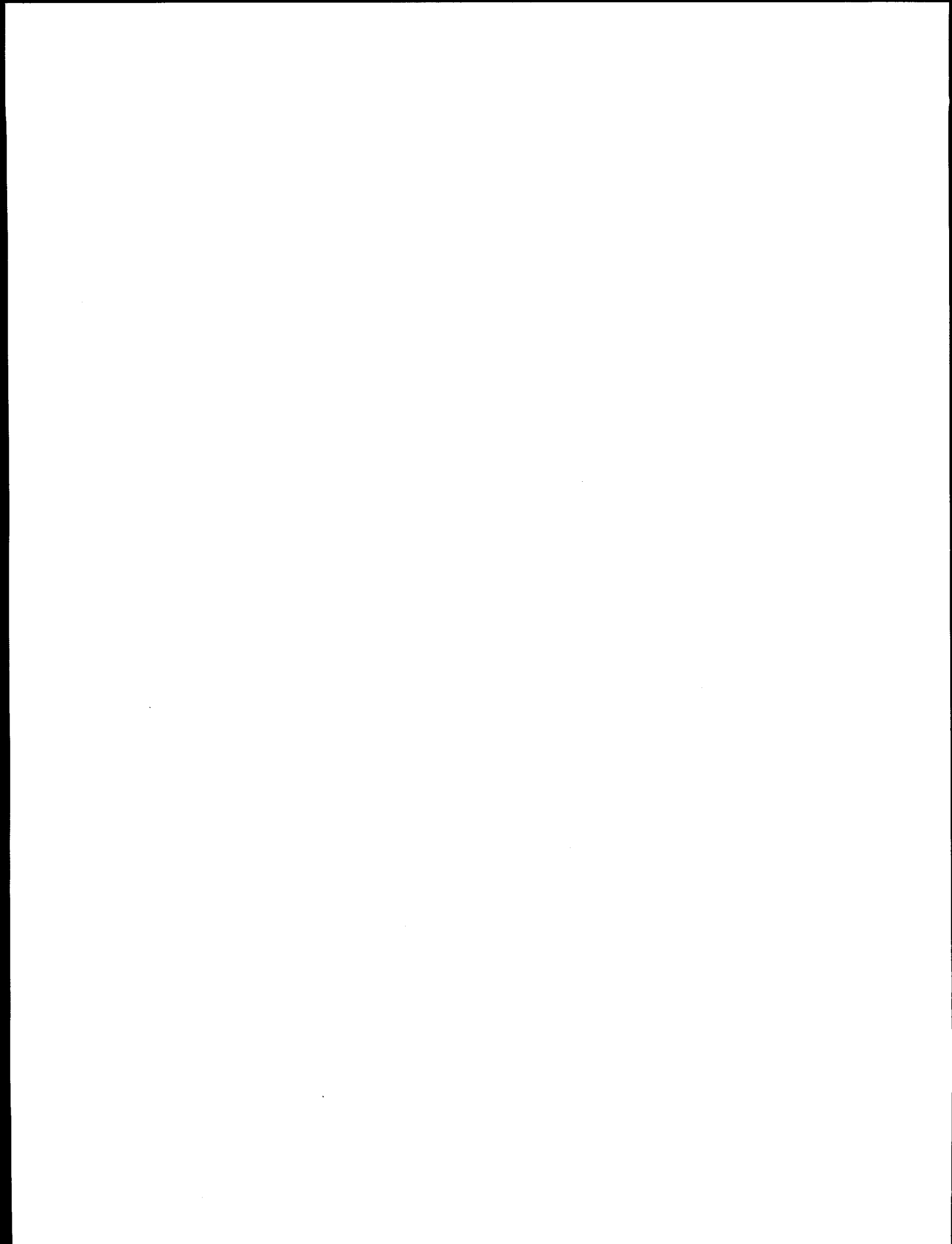
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Engineering and Base Technologies

Molten Salt and Molten Lead Systems Studies

Gary Doolen

Accelerator-driven transmutation of nuclear waste (ATW) is a technology that can essentially eliminate the plutonium, higher actinides, and environmentally hazardous fission products in the spent fuel from nuclear reactors. This project addresses key systems and programmatic issues related to ATW—specifically, how molten salt and liquid lead technologies developed for ATW fit into the waste management infrastructure. We have focused our efforts on modeling and analyzing the physics of the ATW target and blanket to optimize transmutation performance.

First, we defined the active part of the system as consisting of a graphite-reflected, molten salt subcritical blanket assembly coupled to an appropriate liquid lead/bismuth neutron production target. Our system does not have an internal graphite moderator.

Then, we performed preliminary calculations that coupled the neutron transport codes LAHET and MCNP with the depletion codes ORIGEN and DYNA. These calculations showed that our system maintains low actinide inventories while efficiently burning fuel (by fission), two important features. We have also introduced significant passive safety features such as a massive heat sink of liquid salt around the exterior of the reactor vessel.

In addition, we initiated a study to compare our new ATW system with the 8-MW molten salt reactor operated at Oak Ridge National Laboratory during the 1970s to

develop a thorium-uranium breeder reactor. We believe that key features of our system—the accelerator drive, the robust fuel cycle, the low power density, the absence of breeding requirements, and the use of trivalent actinides—should make our ATW system considerably simpler than the Oak Ridge reactor.

Finally, development of effective tools for neutronics calculations, including the coupling of neutron transport, depletion, and kinetic codes, has enabled us to develop innovative designs involving liquid fuels in previously unexplored neutron flux and spectrum regimes. These designs are now feasible through the use of our accelerator drive, which enables us to use subcritical fuel levels for improved control and efficiency. We are continuing to explore the use of a fast neutron spectrum to enhance the efficiency of transmutation.

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Advanced Measurements and Techniques in High Magnetic Fields

Laurence Campbell

The objective of our project was to use advanced measurement technology in order to better understand the fundamental properties of materials subjected to high magnetic fields. Properties of interest included the materials' electrical conductivity, microscopic structure, and thermal characteristics. We had two main tasks: a study of correlated electrons and optical measurements on semiconductors.

In our correlated-electron study, we looked at ground-state properties of heavy fermion compounds in high magnetic fields, with a focus on compounds that exhibit magnetic-field-induced transitions. In particular, we looked at $\text{YbNi}_2\text{B}_2\text{C}$, a new heavy fermion compound presenting extremely high magnetic anisotropy,

which suggested the possibility of having metamagnetic transitions in magnetic fields to 100 T. We also looked at unconventional semiconductors in high magnetic fields, examining the energy-gap formations of Kondo insulator compounds. In particular, we studied the effect that very high magnetic fields have on the energy-gap formation in SmB_6 compounds. Magnetoresistance experiments were performed in magnetic fields to 50 T and at temperatures down to 40 mK. For the first time, we observed that the low excitation gap closes in a magnetic field of 35 T at 40 mK. Studies were also carried out to verify that the observed effects were not sample-dependent and to obtain a theoretical understanding of the phenomena.

In our study of semiconductors, a variety of optical measurements revealed the behavior of semiconductor heterostructures in high magnetic fields. These included measurements of magneto-photoluminescence (MPL) intensity, energy oscillations, and optical Shubnikov-de Haas (OSdH) oscillations in a modulation-doped, GaAs/AlGaAs single heterojunction. The MPL and OSdH measurements showed energy and intensity oscillations caused by the interaction (crossing) between the second sub-band Landau levels (occupied by photo-generated electrons) and the Fermi level. We also looked at MPL measurement of GaAs/AlGaAs double-well structures that included (1) a modulation-doped, coupled double quantum well and (2) an asymmetric, coupled double quantum well. We further looked at undoped GaAs/AlGaAs multiple quantum wells and CdTe single-crystal thin films.

Dynamic High-Strain Deformation of Materials: Experiments, Advanced Constitutive Modeling, and Computational Implementation

Dean Preston

Science-based stockpile stewardship requires the capability to predict the implosion dynamics of primaries and the subsequent expansion of warhead components, for which the properties of material under extreme conditions (large strain, high strain rates, and high temperatures) are critically important. The thrust of this project is directed at providing the Laboratory with the ability to perform predictive numerical simulations of large-strain dynamical behavior by synthesizing material strength and texture data with condensed matter theory and mesoscale physics to construct advanced constitutive models. For this project we have

selected a set of coordinated experimental, mathematical-modeling, and code-implementation tasks that we are using to (1) improve the calibration of the mechanical threshold stress (MTS) and Preston-Tonks-Wallace (PTW) strength models with new Hopkinson bar data at elevated temperatures and at very large strains; (2) extend the models to include texture evolution; (3) employ the methods of molecular dynamics (MD) to improve the models at intermediate strain rates; (4) develop an advanced model of ductile damage growth and spall; and (5) analyze and model solid-solid phase transformations.

Our major accomplishments reflect the coordinated nature of this project. We performed MD simulations of extended-dislocation intersection in face-centered-cubic metals to improve our understanding of plastic deformation at strain rates of 10^4s^{-1} to 10^7s^{-1} . We successfully applied the Tonks ductile damage model to spallation data of ultrapure tantalum. We measured and analyzed the texture and plastic constitutive properties induced by upset forging high-purity bar stock. By reloading prestrained samples over a wide range of temperatures and strain rates to about 10^4s^{-1} , we obtained data required for accurate determination of PTW and MTS model parameters. We modeled the nonequilibrium, shock-induced transformation from the body-centered cubic phase to the hexagonal close-packed phase of iron. To date we have focused the texture evolution modeling on implementing an analytical anisotropic elastoplastic strength model into the CHAD code.

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Ultrasensitive Sensors for Weak Electromagnetic Fields Using HTS SQUIDs for Biomagnetism, NDE, and Corrosion Currents

Edward Flynn

This project centers on developing ultrasensitive sensors for detection of weak magnetic fields and has three task areas: (1) a new concept in superconducting weak-field sensor arrays, (2) introduction of digital signal processors (DSPs) into the superconducting quantum interference device (SQUID) circuit, and (3) improved high-temperature superconducting (HTS) Josephson junctions for HTS SQUIDs.

We have focused on developing HTS (superconducting at liquid nitrogen temperature, 77 K) SQUID sensors and systems, and on background noise rejection using a DSP-controlled flux-locked loop to enable direct cancellation of the noise magnetic field at the SQUID sensor. These efforts have yielded SQUID sensors for applications that require unshielded environments.

We have developed and published the results of a low-performance, prototype electronics system that eliminates 99.5% of a simulated background field in a system integrated with a Los Alamos HTS SQUID. Thus we have improved the background rejection and developed a SQUID sensor system for unshielded applications. We also successfully tested a similar low- T_c system (superconducting at liquid helium temperatures, 4 K).

In addition, we developed better superconducting-normal-superconducting (SNS) junctions to improve both SQUID performance and the mechanics of wire bonding and SQUID circuit layout. A silver-doping technique has significantly improved the performance of the SQUID

devices and increased the production yield. We fabricated and tested SQUIDs with both large-area (1 mm^2) pickup loops for magnetometer applications and those with small-area ($100 \text{ }\mu\text{m}^2$) pickup loops for SQUID microscope applications.

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Short-Pulsed Electric-Discharge Degradation of Toxic and Sludge Wastes

Louis A. Rosocha, Los Alamos National Laboratory

Frank J. Wessel and Vitaly M. Bystritskii, University of California, Irvine

To overcome the drawbacks of conventional pollutant-degradation technologies, we are developing a short-pulsed electric-discharge chemical reactor (see accompanying diagram) to ionize and degrade aqueous-based pollutants, particularly organic compounds such as chlorinated solvents and biphenyls. Such compounds are hazardous air and water pollutants that are harmful to human health. They are not decomposed by natural microorganisms and are, therefore, persistent in the environment. An ideal degradation method would convert these pollutants into harmless or easily handled "mineralized compounds" such as carbon dioxide and simple acids.

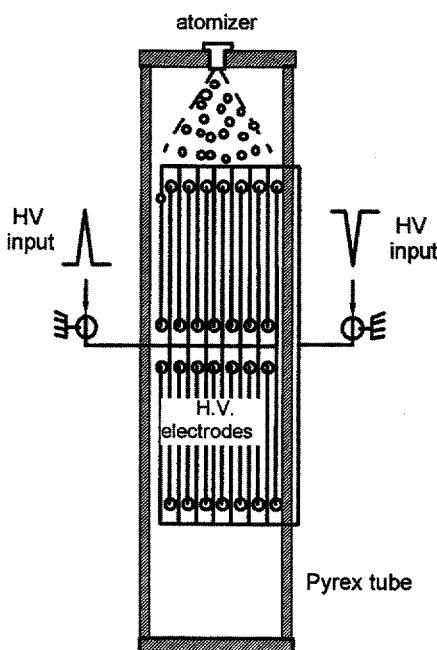
Our reactor offers several advantages over current degradation technologies: it has the potential to produce higher levels of degradation and less secondary waste, and it can handle aqueous-based wastes that are difficult to incinerate. Our degradation process could have widespread use for the treatment of industrial wastes such as those from chemical plants, the petrochemical and pharmaceutical industries, painting operations, and manufacturing.

During the first year of the project, we commissioned the reactor, established its operating parameters (such as voltage and current), and assessed its ability to decompose an aqueous solution of a model organic pollutant, paranitrophenol (pNP). During this second year, we optimized the operating parameters for voltage, pulse duration, pulse-repetition frequency, flow density, and droplet dimension. In addition, we extended the reactor studies to include chlorinated compounds and assembled a new reactor incorporating beneficial design modifications in the chamber-material construction,

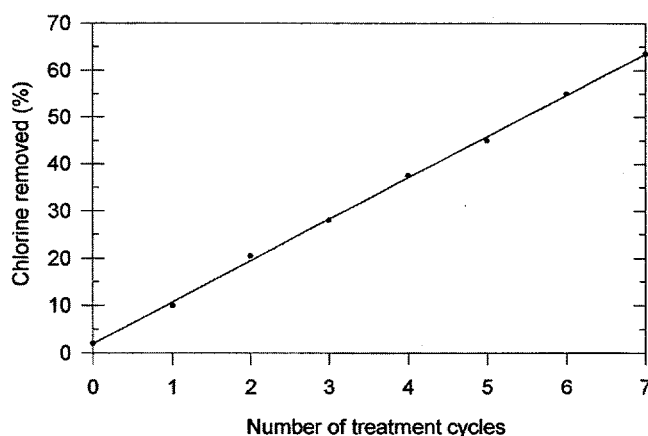
aerosol-injection geometry, electrode geometry, and pulse-discharge circuitry.

We have successfully demonstrated an innovative technique for degrading an aerosol mixture of various organics—pNP, dichlorophenol (DCP), and perchloroethylene—using

a medium-voltage, repetitive, short-pulsed discharge. The accompanying plot shows the data for DCP. The technique provides relatively high electrical efficiency for applications involving waterborne pollutants. The specific energy input for the degradation of one pollutant molecule is in the range of 40–100 eV and depends on both the operational parameters of the discharge and the concentration. We plan to conduct future studies to identify intermediate by-products and to optimize the operating parameters that lead to a higher degree of mineralization.



Cross section of the cell of the short-pulsed electric-discharge chemical reactor.



Plot of the amount of chlorine that the pulsed-discharge reactor removed from a 1000-ppm aqueous solution of dichlorophenol over repeated treatments.

Laser-Sheet Imaging of HE-Driven Interfaces

Robert Benjamin

Interfacial instability of a thin, high-density fluid layer that lies between two less-dense fluids is a fundamental research problem in weapons and inertial confinement fusion (ICF). Experimental observations of highly distorted, preturbulent, shock-accelerated gas flows motivate the study of such flows in liquids.

Our project studies thin liquid layers driven by a high explosive (HE). We are using multiple imaging of laser-sheet illumination (MILSI) to diagnose the transient flow patterns. The objective of our work is to

incorporate MILSI at a Laboratory firing site, enhancing diagnostic capability. This work is supported in both design and data analysis by flow simulations with computer codes used in weapons and ICF work.

Several HE-driven experiments this past year demonstrated the feasibility of producing a useful laser sheet with a 10-W, air-cooled argon laser. The laser beam becomes in effect a thin sheet that illuminates a two-dimensional slice through the liquid interfaces. The resulting image is then detected with a high-speed camera.

For our experiments, we used a fluorescein-loaded layer embedded in water as the test object, and we successfully observed the optical signal from the fluorescein dye. A 10-gal. aquarium contained the experiments.

Other experiments compared two framing methods: pulsed laser versus pulsed camera. The pulsed camera method, which puts an image intensifier on the front end of a charge-coupled-device camera, proved better. We intend to use this method for future HE experiments. Finally, two-dimensional design calculations indicate that diagnostic time will probably be limited by lateral rarefaction waves and that the denser, thin fluid layer should be only 1–2 cm from the HE.

A Neural-Network-Based System for Damage Identification and Location in Structural and Mechanical Systems

Charles R. Farrar

There are many large structures and mechanical systems for which it would be desirable to monitor their "health" and to identify damage as early as possible. The objective of this project is to develop a computer-based system that can remotely monitor and detect damage in structural and mechanical systems. Clearly, such development would be of high value and wide application. We have begun to integrate new damage identification algorithms (that monitor the vibration response of a physical structure or system) with adaptive computing strategies. Our research will couple expertise in

structural dynamics, neural networks, and pattern recognition to develop a comprehensive, self-diagnosing, structural-monitoring and damage-detection system.

Our primary technical achievement this year is the development of nonlinear time-frequency-analysis algorithms that can be applied to measured vibration data for global damage detection in structures and mechanical systems. We have verified these algorithms by applying them to simple test specimens in which the damage produces a nonlinear vibration response not present in undamaged specimens. We are beginning to

adapt these algorithms into a general-purpose computer code that will be used to detect damage in structural and mechanical systems. We have completed a comprehensive literature survey of the damage identification field, and we sponsored a workshop on damage identification from changes in vibration characteristics. Researchers from the United States and many foreign countries attended the workshop and helped to define the state of the art.

Publications

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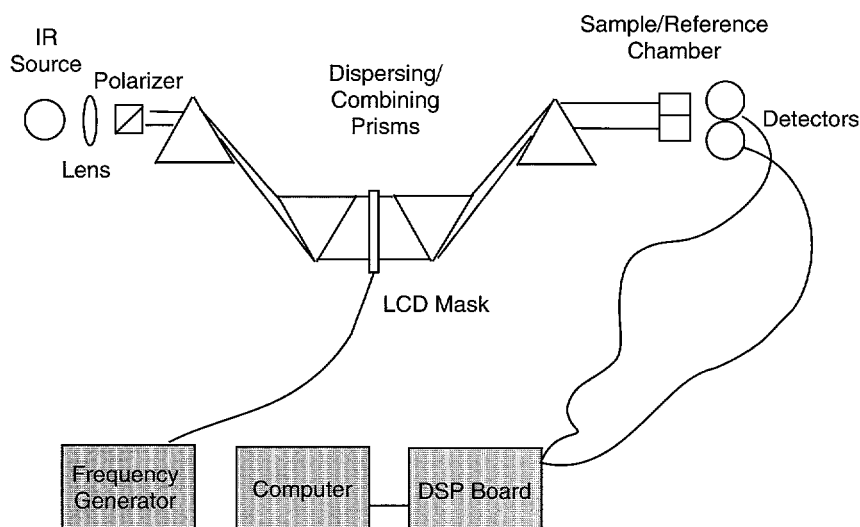
Development of Inexpensive Continuous-Emission Monitors for Feedback Control of Combustion Devices to Minimize Greenhouse Gases, Toxic Emissions, and Ozone-Damaging Products

David J. Funk

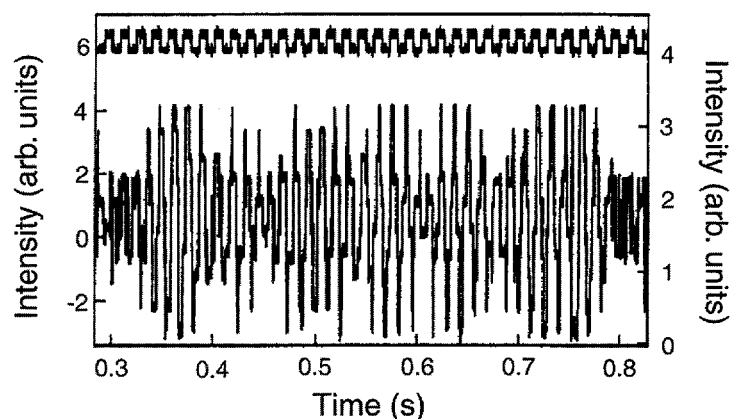
There is little doubt that combustion is the major cause of poor urban air quality and depletion of the ozone layer and a major source of the greenhouse gas carbon dioxide. Furthermore, there is little doubt that global combustion activity is increasing. We are addressing these concerns through research and development of sensitive, inexpensive, continuous-emission monitors (CEMs) based on the optical properties of expected, gas-phase, hazardous materials. To date we have begun work on three specific tasks: (1) proof-of-principle experiments for an inexpensive, solid-state NO_x detector; (2) proof-of-principle experiments of a solid-state, Fourier transform (FT) spectrometer (see the first figure), which has led to a disclosure and pursuit of a patent; and (3) infrared HeNe detection of hydrocarbons. Our preliminary experiments indicate high sensitivity for absorption of the infrared HeNe wavelengths by hydrocarbons found commonly in fuels. We are presently quantifying these results.

We have conducted studies of the solid-state FT spectrometer using a broad-band light source, dispersing the radiation, modulating four bands of light at four different frequencies, recombining the light, and recording the time output in single-shot mode, as shown in the second figure. We applied a Fourier transform to the data and observed the four frequency peaks corresponding to the four bands, as shown in the third figure.

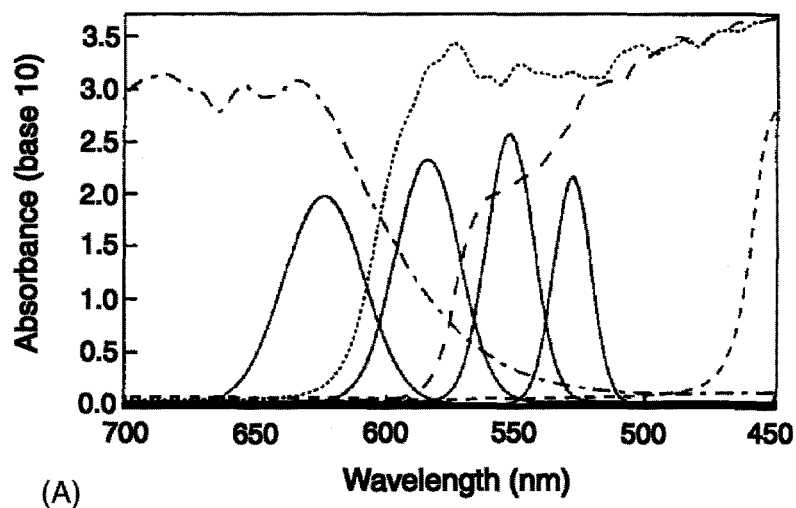
We expect that these inexpensive optical sensors will assist in providing direct feedback of turbine power systems and assure the public and operators of facilities that facility emissions lie within accepted bounds.



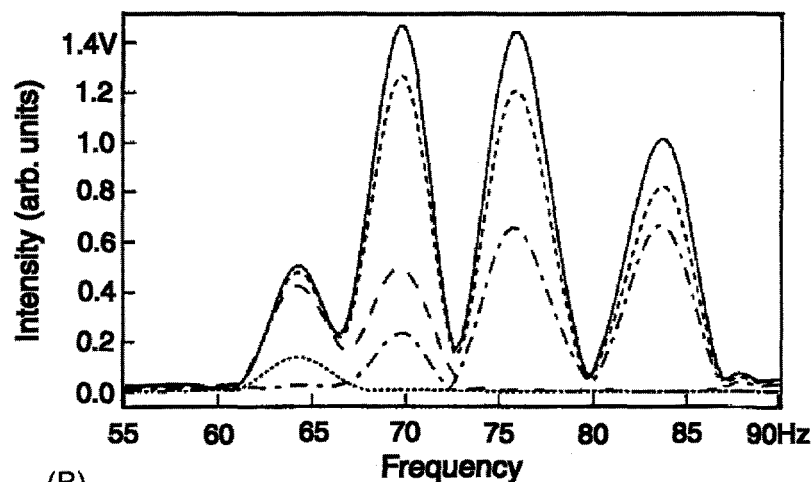
Schematic of the solid-state Fourier transform spectrometer.



Raw output of the phototubes (light detectors) as a function of time. The top trace is the time-dependent signal transmitted through a red filter; only one of the stripes in the mask (the focal plane of an optical system) is transmitting light and only a signal frequency is detected. The bottom trace is the time-dependent signal of the full output from the mask (no filters); the four carriers exhibit the expected beating behavior.



(A)



(B)

Data from studies of the solid-state FT spectrometer. (A) Solid lines are Gaussian fits to the transmission of each of the striped elements. The dashed and dotted-dashed lines are the absorption of each of the filters studied. (B) Transmission spectra of the filters. The solid line is with no filter in place.

Distortion, Residual Stress, and Thermal Gradient Issues for Plutonium Gravity Casting in Ambient-Temperature Molds

S. Dale Soderquist

The goal of this one-year project was to begin development of the process of casting plutonium alloys in thin-walled, ambient-temperature molds and to develop the methods necessary to numerically simulate the process. The new casting technique decreases equipment complexity and increases cooling rates after casting. These effects simplify heat-treating requirements for the plutonium alloys. An additional benefit of the new

process is that it will minimize the amount of waste generated during the casting operation. The numerical methods that were developed to model the process increased understanding and could lead to optimization of the process. Numerical prediction of fluid flow, heat transfer, thermal gradients, stresses, and distortion aids in process design and will eventually allow fabrication of a higher quality product.

During the year we developed a computational model that predicts the distortion and residual stresses in a final cast plutonium part. By numerically tracking the temperature history at different locations in the part, we can estimate the final metallurgical condition of the part. We made several castings to develop information for the model and to develop the mold design. Five of the castings were of surrogate material (four depleted uranium and one bismuth). We made one casting of a plutonium alloy and performed metallurgy on the final part to determine the as-cast material state. Use of a thin-walled mold greatly simplified the casting process, and we expect the metallurgy of the as-cast part to be superior to that of castings made by traditional methods.

Radiation Resistance Measurements of Rare-Earth Permanent Magnet Material for High-Intensity Linac Applications

David Barlow

The objective of this project is to characterize the radiation resistance of rare-earth permanent magnet materials in an accelerator environment by irradiating samples with neutrons. High-strength, rare-earth permanent magnet materials can be used in various compact magnets for steering and focusing high-energy particle beams. Such permanent magnet assemblies take considerably less space than comparable electromagnets and are extremely attractive if space is at a premium. In addition, permanent magnets offer a level of reliability that far surpasses that of electromagnets—an important advantage for applications that require high reliability.

During this reporting period, we exposed samples of samarium cobalt, a rare-earth permanent magnet material, to neutron radiation at the Los Alamos Neutron Science Center A-6 target facility. A total of 20 samples from 4 different sources were exposed to 5 different dose levels ranging from 1.0×10^{17} to 1.0×10^{19} n/cm². We then retrieved the samples from the neutron source and stored them to allow the short-lived activation products to decay. Ten months later, we took the samples out of storage just long enough to measure their relative magnetic moment before returning them to storage.

After exposure, the relative magnetic moment of each sample was found to be within one standard deviation (0.5%) of its preirradiation value. These results indicate no measurable change in the strength of each sample's magnetization. We determined the neutron dose for each exposure by integrating the proton beam on the target and the neutron energy spectrum by analyzing the results of a set of activation foils from a companion experiment at the same facility.

These results indicate that permanent magnet assemblies can survive doses of 1.0×10^{19} n/cm² or more with little or no degradation in their magnetic-field strength. However, in an actual assembly, the permanent magnet material will be exposed to external demagnetizing fields, which have been shown to greatly increase the rate of radiation damage. The real test of a permanent magnet's radiation resistance will require exposing the assembly to the expected radiation field.

Molten Salt and Separations Technologies Evaluation

Francesco Venneri

Accelerator-driven transmutation of nuclear waste (ATW) offers great promise as a method to essentially eliminate plutonium, higher actinides, and environmentally hazardous fission products in the spent fuel waste from nuclear reactors. The goal of this project has been to evaluate the potential of existing technologies and adapt them for use in ATW, focusing on heat generation, fluid motion, and chemical separations for molten salt and lead-based systems.

We have identified significant new methods for preparing spent fuel for ATW treatment and post-transmutation separations and have submitted an application for an international patent

for these processes. Building on the Integral Fast Reactor (IFR) fuel technology processes developed at Argonne National Laboratory and the plutonium pyrotechnology developed at Los Alamos, we have refined the molten salt/liquid metal pyrochemical processes and identified the individual process steps for particular application for ATW. Moreover, we have established a universal process for treating pyrochemical fuel that is applicable to many different types of spent fuel elements and other nuclear waste products.

In addition to molten salt fuels, we have worked on liquid metal fuels, revisiting the bismuth-based fuels

considered by Brookhaven National Laboratory in the past and extending our analysis to lead-based fuels. Molten salt and bismuth-based fuels are especially well suited for the pyrochemical processes under investigation, and these solvents are reusable. Finally, we have modeled and analyzed the thermodynamics of these fuels in state-of-the-art three-dimensional simulations.

This project steadily continues to attract increasing interest from other U.S. national laboratories, industry, and universities.

Publications

Li, N., "Performance Estimates for Waste Treatment Pyroprocesses in ATW" (Second International Conference on Accelerator-Driven Transmutation Technologies and Applications, Kalmar, Sweden, June 3–7, 1996).

Neutron Metrology for Stockpile Stewardship at LANSCE

Chris Morris

The goal of this project is to develop neutron-detector technology to advance research in support of the Laboratory's stockpile stewardship mission. In particular, the emphasis is on higher-resolution imaging detectors for both high-energy and cold neutrons. An additional task is to evaluate new technology for position-sensitive detection of thermal, cold, and ultracold neutrons.

We have made progress in several areas. For example, we have developed and implemented new technology for imaging with high-energy neutrons. We designed and are putting together a detector with an active area of $20 \times 20 \text{ cm}^2$ and a pixel size of $1.8 \times 1.8 \text{ mm}^2$ for neutron radiography. We have coupled converters to image plates and have begun investigating these for fast-neutron imaging. We have designed and are building a

fast, two-dimensional, delay-line-readout, position-sensitive detector for thermal and cold neutrons. Because readout speed is important for ultimate performance, we built a PC-based system aimed at 20 Mbytes/s. We have built two ^3He -doped, wire-chamber systems and have successfully used them for detecting the first ultracold neutrons produced at Los Alamos. We also developed a new concept of a velocity-matched detector for epithermal neutrons and will test it next year.

Publications

Morris, C., V. Armijo, L.G. Atencio, "An Integrating Image Detector for Energy Neutron Radiography" (Fifth International Conf. on Applications of Nuclear Techniques: "Neutrons in Research and Industry," Crete, Greece, June 1996).

Plasmas, Fluids, and Particle Beams

High-Energy Test of Proton Radiography Concepts

Chris Morris

Proton radiography offers the promise of outstanding performance in terms of position-resolution and sensitivity to density variations. Proton radiography is also very well suited to provide a complete history of explosive-driven compressions of heavy-metal systems. In addition, through the use of multiple beams and detector systems, we may be able to reconstruct tomographic images of the object under test. We can also implement proton radiography using established accelerator technology for

beam generation and available test-recording technology for data acquisition. Proton radiography offers potential advantages over current and proposed x-ray radiography technologies and could be an alternative or combined technology for the Advanced Hydrotest Facility (AHF) initiative.

We completed a proof-of-principle experiment for proton radiography using 3- to 9-GeV proton beams available at Brookhaven National Laboratory's Alternating Gradient Synchrotron (AGS). The experiment

produced proton radiographs of a suitably dense, unclassified test object. The experiment tested capabilities in data collection, image reconstruction, and hydro-code simulation and validated models of high-energy proton radiography.

We designed a lens using existing quadrupole magnets, constructed it on the A1 beam line of the AGS, and used it to image 10-GeV protons. The results include (1) images made with an integrating detector, (2) measurements of the background and measurements of the resolution functions, and (3) forward-model fits to the transmission data. In all cases the results agree with initial estimates and provide strong support for the utility of proton radiography as a new hydrotest diagnostic.

Comparison of Cyclotrons and Linacs for High-Intensity-Beam Applications

Tarlochan S. Bhatia

Two types of high-intensity sub-GeV ion accelerators are in use as drivers for neutron sources. The first of these is the linear accelerator, which accelerates up to ~1 mA of 800-MeV protons as operated at Los Alamos. The second class of driver is a cyclotron such as the one at the Paul Scherer Institute in Switzerland, where a beam of ~1 mA of 600-MeV protons is available. The aim of this project is to develop a better understanding of the capabilities and limitations of circular machines in comparison with linear accelerators.

We have conducted a preliminary investigation of the cost benefits of

cyclotrons versus linacs. We find that for applications requiring beam power in the range of 10–20 MW, a cyclotron of high efficiency is probably cheaper than a similar linac of high efficiency because of both the distributed nature of the power feeds in linacs and the significantly lower radio frequency at which a cyclotron operates. In addition, the pulse format of the cyclotron (continuous wave) is naturally better suited to target requirements than a room-temperature linac of high efficiency, which would have to be pulsed to achieve high beam loading. We plan a detailed cost comparison.

We have been looking at the fundamental limits that might restrict the operation of cyclotrons. In particular, we have begun to formulate a halo-formation model analogous to that used by Gluckstern for the treatment of halo in linacs but with the addition of larger external nonlinear terms introduced by the edge focusing in the cyclotron sector magnets. The model formulation is very similar to that in Gluckstern's linac model. The beam-dynamics model of Ryne and Wangler should allow us to simulate halo formation for a high-intensity beam that compares favorably with the linac model.

Finally, we have started to set up detailed simulations for cyclic-ion accelerators with a view toward estimating beam losses not only at extraction but also during acceleration.

A 1-kW-Power Demonstration from the Advanced Free-Electron Laser

Richard Sheffield

Free-electron lasers (FELs) are not widely used because of two principal drawbacks: (1) they tend to be large, complex, and thus costly, and (2) the average power they can deliver in the optical beam is generally low compared with that of other laser sources. As a result, credible use of FELs for high-power applications still requires a demonstration that they can deliver such power. In fact, the highest average power achieved to date with any FEL is only 10 W.

This project was initiated to address the issue of FEL size, which was answered by building the Advanced FEL, a table-top device that demonstrated reliable operation at modest but significant power levels (a few watts). During its operation, we developed a new idea in FEL design that, based on computer simulations, showed would generate as much as

1-kW optical beam power and that would require only minor modifications to the Advanced FEL.

The additional objectives of this project then became to engineer and procure an electron beam line compatible with the proposed operation of a 1-kW optical beam. An associated major task was the physics design of the electron beam line from the end of the wiggler to the electron beam dump. This task was made especially difficult because the beam was expected to have 20 kW of average power and a 25% energy spread.

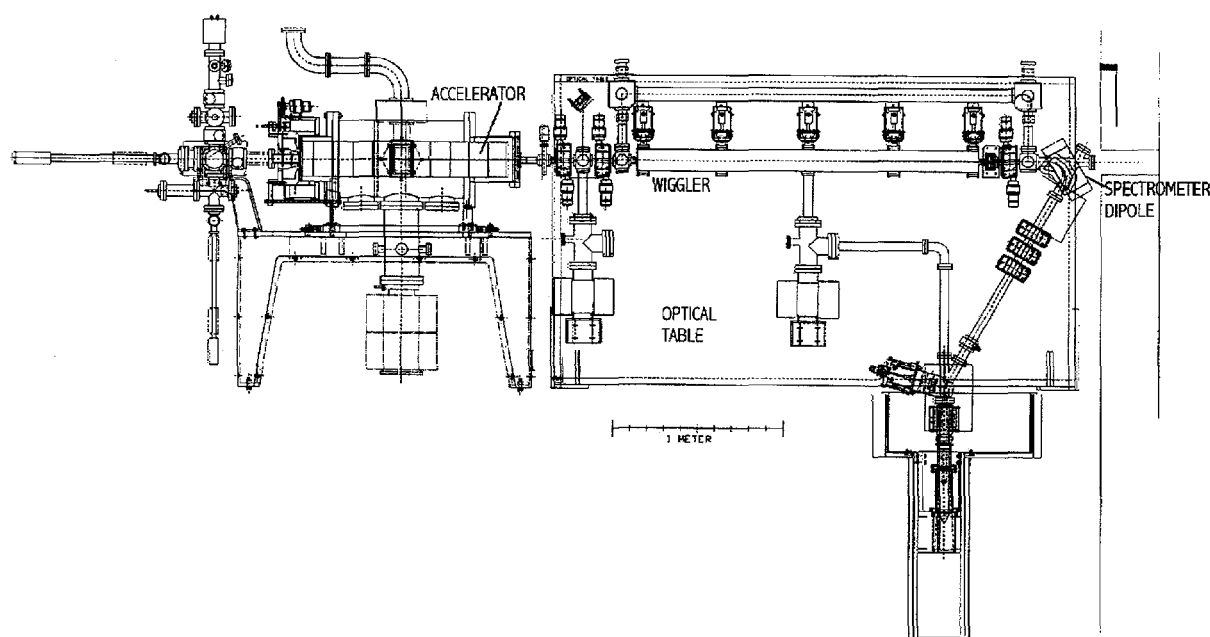
We accomplished all project goals—the high-power electron beam design was completed (see figure), and the hardware necessary for high-power operation was designed and procured. The next step is to test the Advanced FEL at the full 1-kW optical beam power.

Publications

Goldstein, J.C., et al., "Theoretical Study of the Design and Performance of a High-Gain, High-Extraction-Efficiency FEL" (submitted *Nucl. Instrum. Methods Phys. Res.*).

Nguyen, D.C., "Synchronously Injected Amplifiers, a Novel Approach to High-Average Power FELs" (submitted to *Nucl. Instrum. Methods Phys. Res.*).

Sheffield, R.L., et al., "Electron Beamline Design for LANL 1 kW FEL" (submitted to *Nucl. Instrum. Methods Phys. Res.*).



Engineering layout of the high-power FEL beam line at the Advanced Free-Electron Laser facility. The 1.3-GHz linear accelerator is on the left. The optical table is actually a 6-ft-high $\times$ 10-ft-long "wall" on which beam line components, such as the 6-ft-long wiggler, are mounted. The beam line is now fully installed and operational.

Advanced Techniques for Producing, Polarizing, and Storing Ultracold Neutrons

Susan Seestrom

Project objectives are modeling ultracold neutron (UCN) production in cryogenic materials and development of techniques for storing and polarizing ultra-cold neutrons. This activity is centered around developing techniques and experimental apparatus to make use of an UCN source at Los Alamos as well as to study the design and performance of a second-generation UCN source. Such a source is the planned long-pulse spallation source that would provide UCNs of parameters unmatched anywhere else. The techniques being developed will open up a range of fundamental physics studies as well as novel experiments in materials science. Fundamental physics experiments include improved measurement of the neutron lifetime and decay parameters; such measurements provide a sensitive and unique test of the Standard Model for elementary particle interactions.

We have designed and are assembling a UCN transport system and an experimental storage bottle for UCNs. This bottle incorporates a novel shutter design that will allow us to study the spectrum of UCNs produced by the source at the Manuel Lujan Jr. Neutron Scattering Center. The bottle will allow us to study the UCN storage time as a function of different neutron velocity. We have identified and obtained a superconducting magnet suitable for initial attempts to polarize UCNs.

We have designed and are assembling two separate experimental UCN detectors; one is a helium-3 gas scintillator and the other is a helium-3 proportional counter. We have also designed and acquired the components for a data acquisition system that will be used to take and analyze data from these detectors to determine the UCN production rate and the bottle-storage lifetime.

We have written a computer code to calculate the UCN production rate for a solid deuterium superthermal source and compared the results with data taken at the Petersburg Nuclear Physics Institute reactor in Gatchina, Russia. We identified uncertainties in the cross-section databases available as well as the need for better normalization of benchmark data.

Publications

Bowles, T.J., R. Hill, et al., "Ultra Cold Neutrons at a Spallation Source" (Int. Symp. on Neutrons Optics and Related Research, Kumatori, Japan, March 1996).

Seestrom, S.J., T.J. Bowles, et al., "Plans for an Ultra Cold Neutron Source at Los Alamos" (Japan Hadron Project Workshop, Tskuba, Japan, March 1996).

Seestrom, S.J., T.J. Bowles, R. Hill, et al., "Development of an Ultra Cold neutron Source at MLNSC" (Int. Conf. on Applications of Nuclear Techniques, Crete, Greece, June 1996).

Development of Ion-Beam Techniques for the Study of Special-Nuclear-Materials-Related Problems

Carl Maggiore

The objective of this project is to develop ion-beam techniques for characterizing actinides and their effects on other materials. The project is designed to enhance our ability measure the oxidation, corrosion, diffusion, and stability of actinides and the materials with which they may come in contact.

Using ion beams at the Los Alamos Ion Beam Materials Laboratory (IBML) to simulate alpha particles, we have accelerated the aging of polymeric materials in contact with

actinides in engineered systems and under conditions of temperature, pressure, and residual gas composition that correspond to those in the field. We have measured the radiolytic breakdown products of the polymers by mounting a quadrupole mass spectrometer to the scattering chamber at the IBML. We have also determined the depth distribution of hydrogen and helium isotopes in actinides and in surrogates such as the gold/silver alloys used to simulate actinides.

We also evaluated the detection methods required to distinguish between the ions used to probe actinides from the alpha particles produced by natural decay. We have measured the limitations of solid-state detectors for analyzing alpha-active materials and have identified alternative resonance and nuclear reaction methods with time-of-flight detection as preferable when extreme sensitivity is needed for such problems as submonolayer surface contamination. When masking and the use of absorber foils cannot be used to minimize the inherent alpha activity from actinide materials, we have identified particle identification methods for near-surface analysis. We have also measured the sensitivity, spatial and depth resolution, and precision of elastic recoil detection and nuclear reaction analysis in studying actinides.

Generation and Compression of a Target Plasma for Magnetized Target Fusion

Ronald Kirkpatrick

The goal of this project is to develop a computational capability for the design and interpretation of an experiment on magnetized target fusion (MTF). MTF relies on magnetoin insulation to allow slow, near-adiabatic compression of a hot target plasma to fusion conditions.

This year we employed our computational tools to assess the impact of experimental compromises such as a necessary design change in the region near one electrode. We developed a capability to simulate the emission from a hot, magnetized plasma in order to be prepared to interpret pending experimental data in terms of density and temperature, and we tested its effectiveness on the data from related MAGO experiments. For MTF we need to achieve temperatures above 50 eV and magnetic fields above 5 T. In addition, it is necessary to keep impurities at a sufficiently low level to avoid significant radiation losses during the compression phase.

We made significant progress on a new transport method for the computation of alpha-particle energy deposition in the magnetized deuterium-tritium (DT) fusion target plasma. This method will allow efficient computation for the dynamic problems that we must handle for MTF target design. We established informal interactions with the French CEA laboratory, Limeil; Advanced Laser and Fusion Technology, a Canadian company; and General Atomics in La Jolla, California. We are also developing the potential applications of this research to science-based stockpile stewardship.

The first accompanying graph shows a computed Kadomtsev stable profile for a plasma produced by a discharge through a cryogenic deuterium fiber in a 2-cm-high by 2-cm-radius cylindrical container. The calculations indicate that a plasma suitable for MTF can be produced.

The second graph shows the three-dimensional trajectory of a single DT fusion alpha particle through a magnetized target plasma. We are developing a charged particle transport method intended to efficiently and accurately treat energy deposition by the DT alphas in an MTF plasma during fusion ignition and burn.

The third graph represents the temperature history inferred by analysis of filtered silicon diode data from the MAGO II experiment conducted at Los Alamos in October 1994. It suggests that the magnetized plasma reached over 300 eV and remained above 100 eV from 2.5 to 7.5 μ s, after which the diagnostic failed.

Publications

Idzorek, G., and R. Kirkpatrick, "Analysis of Filtered Silicon Diode Data from the MAGO 2 and MAGO 3 Experiments" (to be published in the *Proc. 7th Int. Conf. Megagauss Field Generation, MegaGauss VII*).

Kirkpatrick, R., and D. Smitherman, "Energetic Alpha Transport in a Magnetized Fusion Target" (to be published in *Fusion Technol.*).

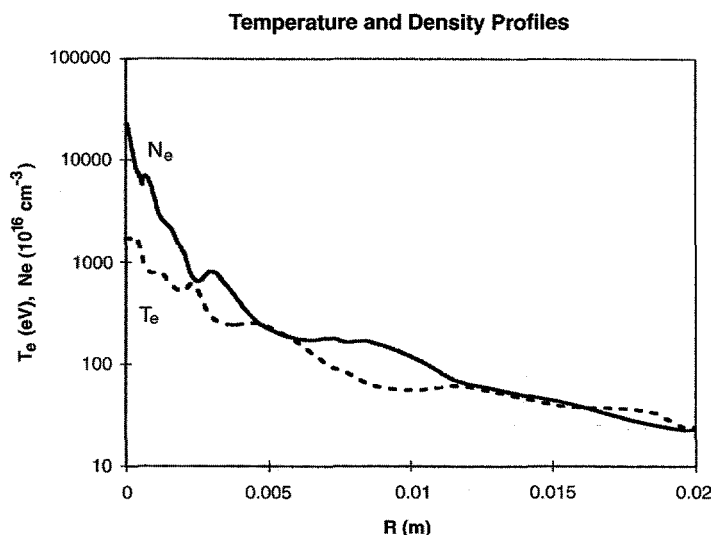
Kirkpatrick, R., P. Sheehey, et al., "Proposed Generation and Compression of a Target Plasma for MTF" (to be published in *Proc. Tenth IEEE Int. Pulsed Power Conf.*).

Lindemuth, I., R. Reinovsky, V.K. Chernychev, et al., "Target Plasma Formation for Magnetic Compression/Magnetized Target Fusion," *Phys. Rev. Lett.* **75**, 1953(1995).

Sheehey, P., R. Faehl, et al., "Computational Modeling of Magnetically Driven Liner-on-Plasma Fusion Experiments" (to be published in the *Proc. 7th Int. Conf. Megagauss Magn. Fields*).

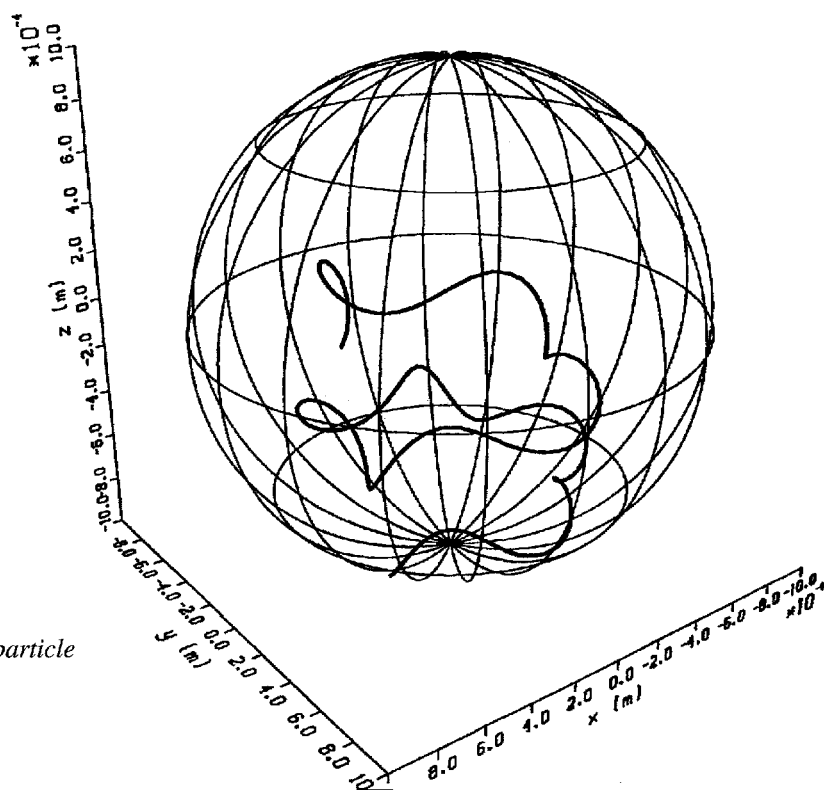
Sheehey P., J. Guzik, et al., "Calculations of Proposed Magnetized Target Fusion Experiments" (to be published in *Proc. 10th Bienn. Nucl. Explos. Des. Phys. Conf.* 1995).

Sheehey, P., J. Guzik, R. Kirkpatrick, et al., "Computational and Experimental Investigation of Magnetized Target Fusion" (to be published in *Fusion Technol.*).

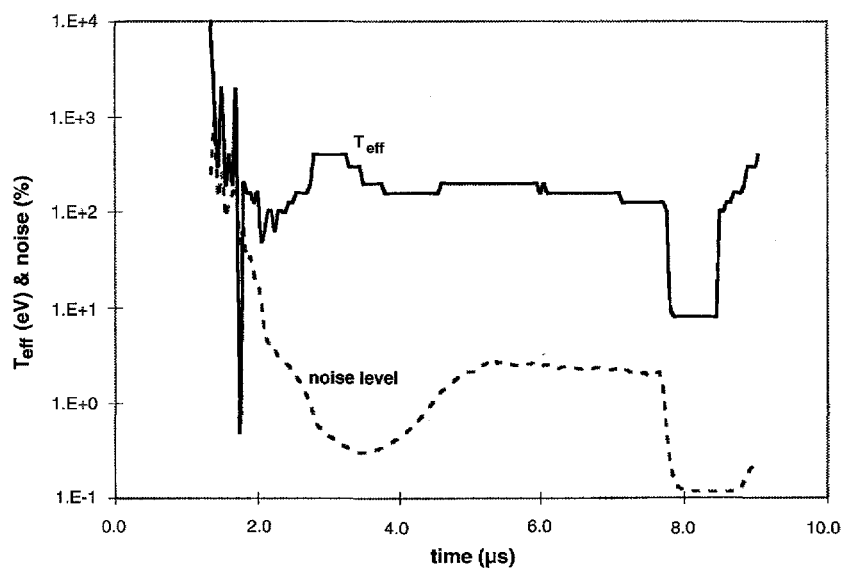


Computed Kadomtsev stable profile for a plasma produced by a discharge through a cryogenic deuterium fiber in a 2-cm high by 2-cm radius cylindrical container.

The trajectory of a single DT fusion alpha particle through a magnetized target plasma.



Effective Plasma Temperature



The temperature history inferred by analysis of filtered silicon diode data from the MAGO II experiment conducted at Los Alamos in October 1994.

Advanced Modeling of High-Intensity Accelerators

Robert Ryne

The goal of this project is to develop an advanced modeling capability for the design of future high-intensity accelerators that can be used for waste transmutation, plutonium conversion, spallation-neutron production, tritium production, etc. Our goal is to develop a suite of codes that can model the beam through kilometers of complex accelerating structures, including radio-frequency quadrupoles, drift-tube linacs, coupled-cavity drift-tube linacs, coupled-cavity linacs, and high-energy, beam-transport sections.

In prior years' work, we developed a family of codes to perform simulations of simple test systems. Now our emphasis has been placed on modeling realistic accelerator systems. Realistic linacs are usually designed and optimized using complex simulation codes. The most widely used linac simulation code in the United States is called PARMILA (for phase

and radial motion in ion linear accelerators). A major accomplishment in our project has been to develop a version of PARMILA that runs on parallel computers, currently the most powerful computers available. The parallel version of PARMILA has significantly improved performance over the original (scalar) version and has been run with up to 30 million particles. In addition, it is more accurate than the scalar version because of the development of a three-dimensional (3-D), as opposed to two-dimensional, parallel space-charge routine.

In another area, we applied split-operator, symplectic techniques to efficiently compute the dynamics of intense beams in radio-frequency accelerating gaps, including complicated z-dependent fields in the gaps.

A third area in which we have made significant progress is in effectively dealing with very large amounts of data. For example, the memory required to store 100 million particles in a 3-D simulation is nearly 10 Gbytes. To handle this volume, we perform "data pruning" inside a code before the data is written to disk. In some cases this process has enabled us to visualize the beam halo while concurrently reducing the size of the data set by more than three orders of magnitude.

Binding Carbon Dioxide in Mineral Form: A Critical Step toward a Zero-Emission Coal Power Plant

Klaus Lackner

Fossil fuels are a large and established energy resource, and coal reserves will last for centuries. However, for fossil fuels to remain an important energy source, the environmental impact of their carbon dioxide emissions must be eliminated. To that end, we are working to develop disposal processes that permanently bind carbon dioxide into environmentally safe, solid waste products, such as carbonate rock. The reason these processes are potentially economically viable is that the underlying chemical reactions are energetically and thermodynamically favored. Last year we published a paper that outlined the basic concepts and sketched out several approaches based on different readily available calcium- or magnesium-bearing minerals and different chemical reaction paths. We are continuing to refine our processing schemes. We are focusing some of our attention on the basic chemistry in an effort to speed up the chemical reaction, thereby making it more cost-effective.

This year we developed several viable processes, selected the most promising candidate processing scheme, and experimentally verified all of the steps in the laboratory. For our candidate process we have improved the reaction rate of the central solid-gas reaction, the carbonation of magnesium hydroxide. We can now achieve rates of carbonation ten times faster than our first experiment appeared to indicate. With regard to alternative processes, we

have tested a wide variety of common minerals for the direct gas-solid reaction with carbon dioxide. We found that either pretreatment or some sort of elevated pressures are necessary to obtain sufficient reaction rates.

By developing this technology, we will provide the fossil power industry with the means to remain competitive, even if greenhouse gases need to be eliminated. Fossil fuels could satisfy a growing world energy demand for many more centuries.

Foreign Nuclear Test Radiochemical Diagnostics

Michael Macinnes

For this project, one of our goals is to develop a capability to interpret radiochemical data from foreign nuclear tests. This ability would be an obvious benefit in non- and counterproliferation and would support the draft language of the Comprehensive Test Ban Treaty. We are also working to develop methods to enhance our ability to extract information from the early nuclear weapons tests of other countries. We are evaluating alternative weapons technologies and improvements to interpretation techniques because these capabilities will be useful in assessing potential proliferant designs.

We can best gain expertise in the evaluation of atmospheric nuclear test

Publications

Butt, D.P., K.S. Lackner, C.H. Wendt, et al., "Kinetics of Thermal Dehydroxylation & Carbonation of Magnesium Hydroxide," *J. Am. Ceram. Soc.* **79**, 1892–1898 (1996).

Lackner, K.S., D.P. Butt, and C.H. Wendt, "Progress on Binding CO₂ in Mineral Substrates" (Third International Conference on Carbon Dioxide Removal, Cambridge, Mass., September 9–11, 1996).

Lackner, K.S., D.P. Butt, et al., "Carbon Dioxide Disposal in Solid Form," *Proc. of 21st Int. Tech. Conf. on Coal Utilization & Fuel Sys.* **21**, 133–134 (1996).

Lackner, K.S., C.H. Wendt, D.P. Butt, et al. "Carbon Dioxide Disposal in Carbonate Minerals," *Energy, Int. J.* **20**, 1153–1170 (1995).

data through manipulating actual radiochemical data. Last year we focused our efforts on a survey of early tests of nuclear weapons states, concentrating on the technology used by most states in their initial nuclear devices. We revived two computer codes that evaluate nuclear test debris on-line, and we trained three analysts to use these and other evaluation tools. This year we used these analysts and tools to evaluate alternative technologies that weapons states might be employing as they expand their technology base and as they incorporate elements of thermonuclear technology. To date, we have reevaluated 10 nuclear events, including those that we selected as benchmarks.

The Characterization of Atmospheric Aerosols: Applications to Heterogeneous Gas-Particle Reactions

Jeanne M. Robinson, Los Alamos National Laboratory
Kimberly A. Prather, University of California, Riverside

We have continued the development of aerosol time-of-flight mass spectrometry for the analysis of the size and chemical composition of individual aerosol particles in real time. We characterized the particles produced directly from various combustion sources such as wood smoke and diesel and gasoline exhaust. The goal of these source-characterization studies is to establish unique size and composition profiles for particles from various sources, which will allow for more-accurate source allocation. Information at this level of detail is necessary for establishing more-directed controls of particulate emissions.

We also built two field-portable instruments for establishing regional variations in aerosol particles, which will add to our understanding of atmospheric processes by probing

different environments in which different chemical processes are expected. We will also use these instruments as on-line probes for monitoring controlled, heterogeneous, chemistry processes important in the stratosphere and troposphere at the single-particle level.

In addition, we have investigated the thermodynamics of model polar stratospheric aerosols. Using second harmonic generation, we monitored the adsorption and phase behavior of HCl on water ice films. We identified the quasi-liquid/solid transition postulated by theorists. We are presently using mass spectrometry to measure vapor pressures over the hydrate ice films in conjunction with optical measurements, as shown in the figure. Our goal is to map out the phase diagram of the HCl/H₂O system

as a function of temperature, pressure, and surface coverage.

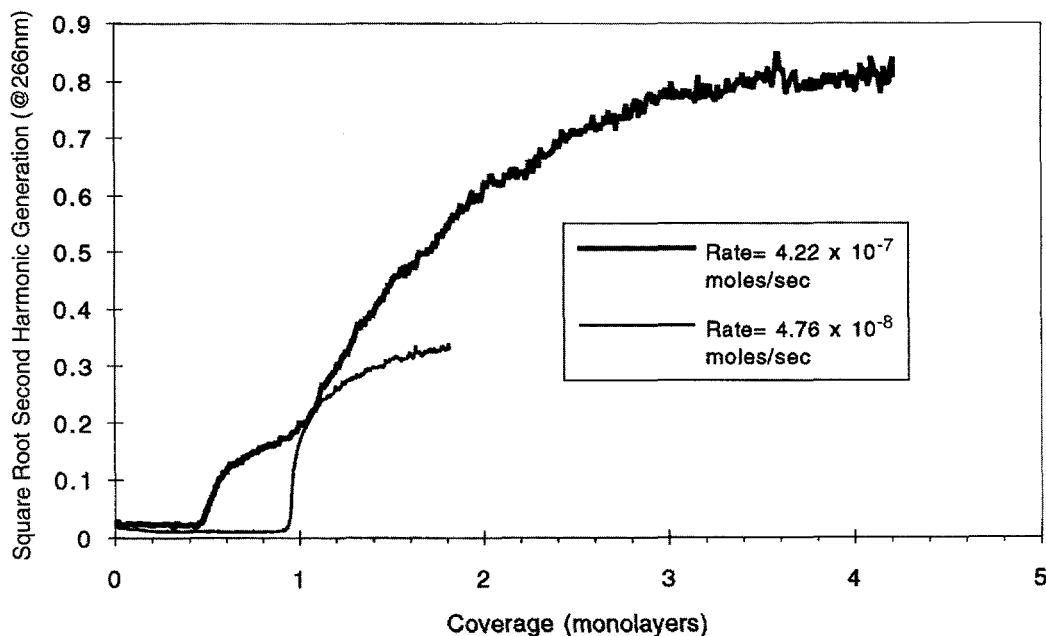
Publications

Henson, B.F., K.R. Wilson, and J.M. Robinson, "Quantitative Measurements of Multilayer Physical Adsorption on Ice from Nonlinear Light Scattering" (1996 International Symposium on Physics and Chemistry of Ice, Hanover, N.H., August 1996).

Noble, C.A., and K.A. Prather, "Real-Time Measurement of Correlated Size and Composition Profiles of Individual Atmospheric Aerosols," *Env. Sci. Tech.* **30**, 2667 (1996).

Wilson, K.R., B.F. Henson, and J.M. Robinson, "Physical Adsorption Measurements of HCl on Water Ice," *EOS Trans., Am. Geophys. Union* **76** (1995).

Wilson, K.R., B.F. Henson, et al., "Equilibrium Thermodynamics of HCl Adsorption on Water Ice" (211th American Chemical Society National Meeting, New Orleans, La., March 1996).



Adsorption spectra for HCl on water ice at 180 K. The HCl vapor was introduced at two different rates. Our preliminary data analysis using classical physical adsorption suggests that different hydrates are formed in these experiments.

Kinetic Studies of Competitive Adsorption Processes Related to Automobile Catalytic Converters

Mark Paffett, Los Alamos National Laboratory
Francisco Zaera, University of California, Riverside

This project focuses on the study of the reaction kinetics in catalytic conversion processes for exhaust gases by using the method devised by King and Wells. We have investigated both the oxidation of CO and the reaction between NO and propene on Pt(III) surfaces.

We found that in the first case, the presence of preadsorbed atomic oxygen does not significantly affect the initial sticking coefficient of CO, but preferentially blocks the bridge sites. No reaction takes place below 300 K, and above 400 K, CO₂ production is controlled by the impinging frequency of the incoming CO. However, between 300 and 400 K, the rate of surface recombination of CO with oxygen competes with that of CO adsorption, and not all of the surface oxygen is reactive.

The behavior observed in that latter regime suggests that the reactivity of the adsorbed oxygen depends on the local coverage of neighboring sites. Beams with CO + O₂ mixtures were also used to better mimic realistic catalytic conditions. We found that at high temperatures, the rate of CO oxidation is equally determined by the CO incoming flux as long as the CO:O₂ ratio is kept low. For high CO:O₂ ratios, however, the CO steady-state coverage increases, poisoning the adsorption of oxygen and slowing down the overall CO₂ production.

Finally, preliminary data has now been acquired for the second system (NO and propene) and is being analyzed.

Publications

Liu, J., M. Xu, and F. Zaera, "Determination of the Rate Limiting Step in the Oxidation of CO on Pt(III) Surfaces," *Catal. Lett.* **37**, 9–13 (1996).

Liu, J., M. Xu, et al., "Sticking Probabilities for CO Adsorption of Pt(III) Surfaces Revisited," *J. Phys. Chem.* **99**, 6167–6175 (1995).

Xu, M., J. Liu, and F. Zaera, "Kinetic Evidence for the Dependence of Surface Reaction Rates on the Distribution of Reactants on the Surface," *J. Chem. Phys.* **104**, 8825–8828 (1996).

Zaera, F., J. Liu, and M. Zu, "Isothermal Study of the Kinetics of Carbon Monoxide Oxidation on Pt(III): Rate Dependence on Surface Coverage" (submitted to *J. Chem. Phys.*).

Investigations of Biomimetic Light-Energy-Harvesting Pigments

Robert Donohoe

The design of materials for controlled photophysical response, such as energy conversion or destruction of pollutants, can be approached from a molecular level. The goal of this project is construction of extended arrays of molecular pigments with predictable and controllable light-initiated responses.

We have approached the investigation of the excited-state dynamics in porphyrin oligomeric arrays by acquiring transient absorption and time-resolved fluorescence measurements. The present effort serves as a complement to these excited-state methods by using resonance Raman, electron paramagnetic resonance, and

absorption spectroscopies to characterize the ground-state structures of the neutral and oxidized porphyrin arrays. The electrochemical and spectral properties of the arrays indicate that the electronic communication between the macrocycles is relatively weak in the ground and excited electronic states. This communication is through-bond, rather than through-space, and is mediated by the diarylethylene linker.

In the case of the torsionally unconstrained dimers, we observed extremely large resonance Raman intensity enhancements for aryl ring and ethyne-bridge stretching modes. These intensity enhancements are

attributed to an excited-state conformational change that enhances the conjugation between the p-electron systems of the porphyrin ring and bridging diarylethylene group. The intensity of the aryl and ethyne-bridge vibrations monotonically decreases as the degree of steric constraint increase. This trend parallels that observed for the rates of energy transfer in these arrays and indicates that the excited-state electronic communication can be tuned via structural modification of the diarylethylene linker.

We are about to begin the investigation of new arrays that incorporate redox switches to mediate energy transfer. These switches may include pigments capable of selective oxidation or, possibly, chromophores that can be photo-oxidized, thereby providing a light switch of the excited-state energy transfer.

Mathematics and Computational Sciences

Nuclear Futures Analysis and Scenario Building

Edward D. Arthur

In this project we have begun examination of future nuclear-energy scenarios and assessed the size of the resulting inventories of plutonium and other nuclear materials. We also modeled various technological approaches and their impacts on the management of such inventories. The effort emphasizes establishing quantitative metrics to assess proliferation risk from projected material accumulations during civilian nuclear-power use. Principal focuses of these analyses are identification and testing of technologies and materials management strategies that contribute positively to future security, nonproliferation, and robust-energy scenarios.

We accomplished the following objectives in FY 1996. (1) A robust nuclear-fuel-cycle model was added to a major global energy, economics, energy-projection model (i.e., the Pacific Northwest National Laboratories' Edmunds, Reilley, and Barnes model) and the results tested. These results provide unique capabilities for assessing and testing nuclear materials-management strategies for nine major world regions. The accompanying figure provides an example of projected growth in global plutonium inventories (arising from spent nuclear reactor fuel) along with regional contributions to the total. We also developed a more detailed nuclear-fuel-cycle model to be used separately that provides a platform for testing the energy model results and for technology impact assessment (see item 3). (2) We developed a model to determine proliferation-risk metrics associated

with the civilian nuclear-fuel cycle and began testing plutonium management strategies. (3) We modeled three technologies for management of global plutonium inventories—mixed-oxide-fueled light-water reactors, liquid-metal reactors, and accelerator systems—via the code system of item 1 and assessed the impacts in terms of residual-plutonium inventories, time period to achieve results, and the system deployments required.

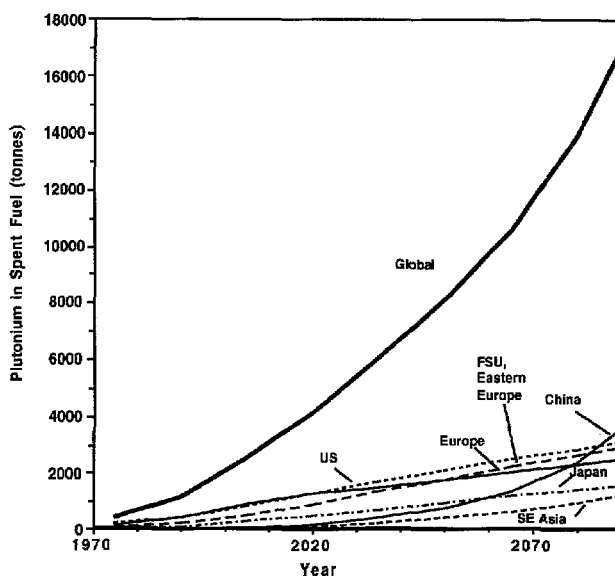
Publications

Arthur, E.D., "Impact of ADTT Concepts on the Management of Global Plutonium Inventories" (Second Int. Conf. on Accelerator-Driven Transmutation Technologies and Applications, Kalmar, Sweden, June 3–7, 1996).

Arthur, E.D., and R.L. Wagner, "The Los Alamos National Laboratory Nuclear Vision Project" (Global Foundation Energy Conf.; Technology for the Global Economic and Environmental Survival and Prosperity, Miami Beach, Fla., Nov. 8–10, 1996).

Krakowski, R.A., "Global Nuclear Energy/Materials Modeling in Support of Los Alamos Nuclear Vision Project" (Global Foundation Energy Conf. Technology for the Global Economic and Environmental Survival and Prosperity, Miami Beach, Fla., Nov. 8–10, 1996).

Krakowski, R.A., "Long-Term Tradeoffs between Nuclear-Fossil-Fuel Burning" (Global Foundation Energy Conf.; Technology for the Global Economic, Environmental and Survival and Prosperity, Miami Beach, Fla., Nov. 8–10, 1996).



Results for projected plutonium inventories in spent reactor fuel arising from use of the energy-projection and nuclear-fuel-cycle model discussed in the text.

New Numerical Models for Global Ocean Modeling

Len Margolin

We have developed new numerical methods that improve the accuracy and efficiency of models of geophysical flows, especially models of the global circulations of the ocean over climate time scales. We adapted analytical techniques from nonlinear dynamics and nonequilibrium statistical mechanics to develop these methods. We developed new algorithms based on these methods in a format compatible with the current generation of ocean models, and we implemented these algorithms on a variety of platforms, including workstations and the massively parallel Connection Machine, CM-5.

Specifically, we constructed an approximate inertial manifold methodology for finite-difference and finite-volume approximations, and generalized the underlying theory to include both dissipative and quasi-geostrophic flows; we developed a

method of averaging for multiple-time-scale problems; and we implemented a semi-Lagrangian formulation of the dispersive shallow-water equations. We constructed numerical models for Burgers' equations in one and two dimensions and for a 1.5-layer model of shallow and dispersive shallow water (to simulate ocean basin circulations).

After formulating and implementing our new algorithms, we tested them on problems representative of large-scale ocean dynamics. We applied singular spectrum analysis (SSA) to compare the time spectra of the numerical solutions of the two 1.5-layer models. Similarly, we used the principal orthogonal decomposition (POD) to compare the spatial accuracy of these different approximations. We demonstrated that the new models would reproduce the accuracy (in space and time) of more finely resolved simulations, but at a

reduced cost of computer time and memory. We believe this is the first application of SSA and POD, which were designed for experimental data analysis, to compare the accuracy of different numerical realizations of stochastic flows.

We have presented our results at professional meetings in the fields of applied mathematics, computational physics, and meteorology and have published these results in appropriate peer-reviewed journals.

Publications

Nadiga, B.T., L.G. Margolin, and P.K. Smolarkiewicz, "Different Approximations of Shallow Fluid Flow over an Obstacle," *Phys. Fluids* **8**, 2066 (1996).

Nadiga, B.T., M.W. Hecht, et al., "On Simulating Flows with Multiple Time Scales" (submitted to *Theor. and Comput. Fluid Dyn.*).

Poje, A.C., D.A. Jones, and L.G. Margolin, "Enslaved Finite Difference Approximations for Quasi-Geostrophic Flow," *Physica D* **98**, 559 (1996).

Lie Group Applications to the Solution of Differential Equations

Charles W. Cranfill

This project applies Lie Group techniques to the solution of partial differential equations (PDEs) describing physical systems important to Los Alamos National Laboratory's scientific mission. There are two main objectives: (1) to construct analytic or quasi-analytic solutions for use as benchmark test problems and (2) to develop improved numerical solution algorithms that possess the same symmetries (e.g., rotational, translational, and scaling invariance) as the PDEs.

This year we developed a general procedure for finding analytic solutions to the hydrodynamic equations for fluids having more realistic equations of state than that of an ideal gas. The procedure was used to construct analytic solutions to the one-dimensional Noh test problem, which describes an imploding fluid whose stagnation against a symmetry surface produces an outward-moving shock, for both the stiff-gas and Mie-Gruneisen equations of state.

We also constructed an analytic solution to the Sedov test problem,

which describes the spherical blast wave produced by a point explosion, for the case in which the ambient gas has an initial density gradient in a given direction. This provides a two-dimensional generalization of the usual one-dimensional solution.

Publications

Axford, R.A., "Group Theory of Invariant Flux and Slope Limiters" (Ninth Nuclear Explosives Code Developers Conf., San Diego, Calif., Oct. 22-25, 1996).

Axford, R.A., "Lie Group Symmetry Properties of the Besnard-Harlow-Rauenzahn-Zemach Spectral Turbulence Transport Model" (JOWOG-32M Mtg. on Mix Research, Los Alamos, N.Mex., July 22-26, 1996).

Lithospheric Processes

W. Scott Baldrige

Our objective was to improve our understanding of the origin and evolution of the lithosphere by studying selected processes such as deformation and magmatic intrusion during crustal extension, formation and extraction of mantle melts, fluid transport of heat and mass, and surface processes that respond to deep-seated events. Additional objectives were to promote and develop innovative techniques and support relevant educational endeavors.

Our seismic studies suggest three central points: (1) that underplating of crust by mantle melts is an important crustal-growth mechanism, (2) that low-angle faults can be seismogenic, and (3) that shear deformation creates mantle anisotropy near plate boundaries. Results of geochemical work determined that magmas from oceanic intraplate islands derive from a uniform depth in the upper mantle, whereas melts erupted at mid-ocean ridges are mixed from a range of

depths. We determined the extent and style of fluid infiltration and trace-element distribution in natural magmatic systems, and we investigated neon-21 as a tool for dating surficial materials.

Publications

Ferguson, J.F., W.S. Baldrige, L. Braile, et al., "Structure of the Española Basin, Rio Grande Rift, New Mexico, from SAGE Seismic and Gravity Data," *New Mex. Geol. Soc. Guidebook* **46**, 105–110 (1995).

Jiracek, G.R., C.L. Kinn, C.L. Scott, et al., "Tracing Crustal Isotherms under the Western Margin of the Jemez Mountains Using SAGE and Industry Magnetotelluric Data," *New Mex. Geol. Soc. Guidebook* **47**, 129–133 (1996).

Olsen, K.H., "Continental Rifts: Evolution, Structure, and Tectonics," in *Developments in Geotectonics* (Elsevier, Amsterdam, 1995), vol. 25, pp. 453–460.

Sims, K.W., W. DePaolo, D.J. Murrell, et al., "Mechanisms of Magma Generation beneath Hawaii and Mid-Ocean Ridges: U-Th and Sm-Nd Isotopic Evidence," *Science* **267**, 508–512 (1995).

Slack, P.D., P.M. Davis, W.S. Baldrige, et al., "The Upper-Mantle Structure of the Central Rio-Grande Rift Region from Teleseismic P-Wave and S-Wave Travel-Time Delays and Attenuation," *J. Geophys. Res., Solid Earth* **101**, 16003–16023 (1996).

Wendlandt, E., D.J. DePaolo, and W.S. Baldrige, "Thermal History of Colorado Plateau Lower Crust from Sm-Nd Mineral Geochronology of Xenoliths," *Geol. Soc. Am. Bull.* **108**, 757–767 (1996).

White, T.D., G. Suwa, and B. Asfaw, "*Australopithecus Ramidus*, a New Species of Early Hominid from Aramis, Ethiopia," *Nature* **375**, 88 (1995).

WoldeGabriel, G., et al., in "Scientific Correspondence," reply to "Age of Early Hominids," *Nature* **376**, 559 (1995).

Geometrically Compatible 3-D Monte Carlo and Discrete-Ordinates Methods

Jim Morel

The first objective of this project was to develop a discrete-ordinates (S_n) radiation transport code for calculating three-dimensional (3-D), unstructured, tetrahedral meshes. The second objective was to develop variance reduction techniques for the general-geometry Monte Carlo Neutron and Photon (MCNP) transport code that would utilize adjoint solutions from the unstructured-mesh S_n code. Our S_n code was the first 3-D unstructured-mesh S_n code ever developed. As such, it

provides us with a unique capability for efficiently and accurately performing calculations in complex 3-D geometries. In addition, this S_n code can generate adjoint solutions which can be used by the MCNP code to dramatically reduce the statistical variance obtained in difficult calculations.

In the past year, we investigated new iterative acceleration techniques for our S_n code; investigated automatic mesh refinement techniques for our S_n code; tested the accuracy and

cost of the code by modeling neutron-based oil-well logging tools; and generated adjoint solutions used in the testing of a new Monte Carlo variance reduction technique called the local importance function transform. The latter technique was developed by our collaborators at the University of Michigan.

Adaptive Monte Carlo Methods for Radiation Transport

Thomas E. Booth

For discrete-transport problems, exponential convergence can be obtained either by learning the zero variance biasing (adaptive Monte Carlo) or by repeatedly solving for the difference between the true solution and the current estimate of the solution (reduced-source Monte Carlo). This project seeks to generalize these known exponential-convergence methods from discrete-transport problems to continuous-transport problems. The ultimate goal is to apply these methods to problems that currently cannot be solved.

The project sought to produce the first exponential-convergence results for continuous Monte Carlo problems, either by adaptive or reduced-source Monte Carlo. Additionally, we sought to understand and protect against false convergence. We successfully showed adaptive Monte Carlo to produce exponential convergence (with computer time) on a bidirectional, continuous-transport problem with arbitrary scattering, as shown in the first figure. We extended the results to K-directional problems and tested for $K = 10$.

The solution method used the differential transport equation to constrain the possible solutions to a $2K$ -parameter family. Statisticians have proved exponential convergence for such families on discrete problems. The false convergence problem was ameliorated by enforcing local constraints on the biasing. That is, although the global solution is not

known, the local characteristics of the solution are known, and the global solution must be locally consistent.

The reduced-source method produced exponential convergence for a unidirectional problem with pure absorption, as shown in the second figure. Expressing the reduced source as an expansion of continuous-basis functions seems to offer the best hope for extending the exponential convergence to multidimensional problems with scattering.

Publications

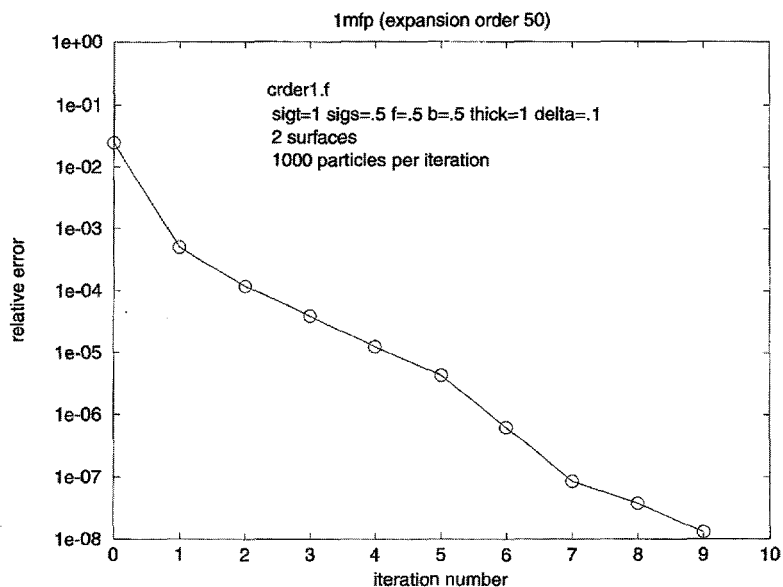
Booth, T.E., "Adaptive Monte Carlo Attempts on a Continuous Transport Problem" (The Adaptive Monte Carlo Workshop, August 14–16, 1996, Los Alamos, N.Mex.).

Booth, T.E., "Exponential Convergence on a Continuous Monte Carlo Transport Problem" (submitted to *Nucl. Sci. Engin.*).

Kong, R., and G. McKinney, "Error Reduction Using Adaptive Monte Carlo: The Reduced Source Method" (The Adaptive Monte Carlo Workshop, August 14–16, 1996, Los Alamos, N.Mex.).

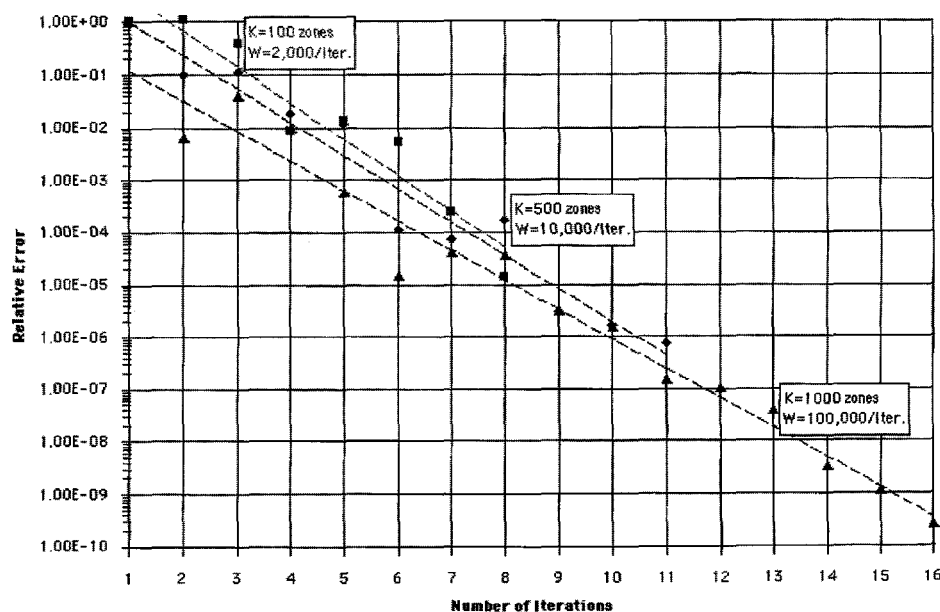
Lichtenstein, H., "Investigation of False Learning in Adaptive Monte Carlo Transport" (The Adaptive Monte Carlo Workshop, August 14–16, 1996, Los Alamos, N.Mex.).

Exponential Convergence by Taylor Expansion



Plot of the relative error of the penetration probability through a slab with bidirectional scattering as a function of iteration number (1000 particles per iteration).

Plot of the relative error versus iteration number for penetration through a 5-mean-free-path, purely absorbing slab, using the reduced-source method. Different values of the particles per iteration (W) and number of slab zones (K) are shown.



High-Performance Computing of Electron Microstructures

Alan Bishop

The purpose of this project, a collaboration with scientists at the University of California at Santa Barbara (UCSB), is to model novel quantum properties of optically driven, electronic nanostructures (quantum wells). These structures are fabricated and measured at UCSB using dedicated molecular-beam epitaxy and free-electron laser facilities. We have developed a new time-dependent density-functional model that is being implemented in large-scale parallel computations and that can systematically handle all the relevant physical interactions in nonequilibrium properties. This model is helping us understand the nanostructures' response to optical excitation.

We extended our model with a density matrix formalism that incorporates dephasing and energy relaxation processes. We also generalized the formalism and numerical implementation to include multiple quantum-level processes. We then used this robust model to simulate a

bifurcation sequence in a quantum well. Our simulation agrees with preliminary experimental measurements and points the way to designing optical devices with technologically important frequency-mixing and subharmonic responses. Finally, we developed a theory of nonequilibrium transport in a double quantum-dot system.

Our project draws on the Laboratory's core competency in theory, modeling, and high-performance computing. It is relevant to programs in nanotechnology, semiconductor modeling, information and sensor technology, and multiscale nonlinear and nonequilibrium processes.

Publications

Bewley, W.W., C.L. Felix, J.J. Plombon, et al., "Far-Infrared Second-Harmonic Generation in GaAs/AlGaAs Heterostructures: Perturbative and Nonperturbative

Response" (to be published in *Phys. Rev. B*).

Birnir, B., V. Gudmundsson, and K. Johnson, "Floquet States and Electron Interactions for Laser-Driven Quantum Wells" (submitted to *Phys. Lett. A*).

Galdrikian, B., and B. Birnir, "Period Doubling and Strange Attractors in Quantum Wells," *Phys. Rev. Lett.* **76**, 3308 (1996).

Kenkre, V.M., S. Raghavan, et al., "Memory Function Approach to Interacting Quasiparticle Boson Systems," *Phys. Rev. B* **53**, 5407 (1996).

Wang, L., W.Z. Wang, and A.R. Bishop, "Theory of Quantized Dynamic Capacitance Charging Spectroscopy in Nanostructures," *Phys. Rev. Lett.* **74**, 4710 (1995).

Zang, J., A.R. Bishop, et al., "Nonequilibrium Transport and Population Inversion in Double Quantum Dot Systems" (to be published in *Int. J. Mod. Phys.*).

Modeling Complex Phenomena: Multiple Length and Time Scales in Extended Dynamical Systems

Peter Lomdahl

This research combines competencies in high-performance computing, theory of complex systems, and materials science in a new way that has great potential for applications to multiple length- and time-scale phenomena in condensed matter and materials science. We are developing (1) analytical techniques in non-equilibrium and nonlinear science and (2) numerical algorithm and simulation techniques using massively parallel computation and advanced visualization. We then apply the developed techniques to the study of mesoscopic textures and their associated dynamics for a number of

topical problems in materials science and condensed matter. The mesoscopic scale provides a fundamental bridge between microscopic and macroscopic modeling approaches and, ultimately, is the link between (1) synthesis and processing and (2) functionality.

Using nonlinear techniques and large-scale simulations, we have systematically studied mesoscale pattern formation and dynamics in nonlinear, nonequilibrium systems exhibiting topological excitations (i.e., dislocations, vortices, vortex lines, and domain walls). Specifically, we have focused our research efforts on the following:

- dislocation generation from crack fronts in ductile materials;
- the smoothing of rough surfaces in solid-on-solid models;
- ordering and melting of moving flux lattices in three-dimensional Josephson junction arrays with disorder and external magnetic field and current;
- filamentary and plastic vortex flow in disordered thin-film superconductors;
- magnetic vortices in Heisenberg spin layers; and
- hierarchical twinning and tweed texture in elastic models.

Publications

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Dominguez, D., N.G. Jensen, and A.R. Bishop, "Resistive Hysteresis and Nonlinear J-V Characteristics," *Phys. Rev. Lett.* **75**, 4670 (1995).

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Jensen, N.G., A.R. Bishop, and D. Dominguez, "Metastable Filamentary Vortex Flow in Thin Film Superconductors," *Phys. Rev. Lett.* **76**, 2985 (1996).

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Zhou, S.J., D.M. Beazley, P.S. Lomdahl, et al., "Dislocation Emission from a Three-Dimensional Crack" (submitted to *Proc. 9th Int. Conf. Fracture*).

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Continuing Benchmarking of Ocean-Circulation Models

David Poling

Our objectives in this project were to (1) become proficient at running ocean- and climate-related simulation codes and analyzing their outputs, (2) use this proficiency to follow the migration of simulation to massively parallel computers, and (3) communicate the lessons we learn to our colleagues and coworkers.

This year we completed a series of ensemble runs using two computer codes: one that simulates the atmosphere, the other the ocean (ECHO). These runs of the ECHO-coupled, ocean-atmosphere model should provide insight into using computer models to predict climate changes. The resulting amount of data will be immense and take some time to analyze.

The 100-year run will provide a baseline for comparisons of ocean and

atmosphere simulations for years to come. Analysis of this run will provide insight into the strengths and weaknesses of such simulations and better understanding of the subgrid processes that will always be necessary in such calculations. The ensemble runs should provide one of the first attempts to study the variability of this kind of simulation and thus a means of evaluating the predictive capability of any such simulation.

Publications

"Preliminary Results from Ensemble Runs of the ECHO-Coupled, Ocean-Atmosphere Model" (Cooperative Antarctic Research Center, University of Tasmania, Hobart, Australia, July 29, 1996).

Simulation Methods for Advanced Scientific Computing

James Gubernatis

The rapid increase in raw computational power has created exciting opportunities for scientific computation. The complexity and realism of the problems that can be simulated promise to greatly advance many scientific and technological fields. Accordingly, scientific computing is enjoying considerable worldwide popularity. Yet many challenging scientific problems remain unsolved because of inadequate algorithms, especially algorithms that are suitable for massively parallel architectures.

In this project, our objective is to create effective new algorithms for solving these problems, giving the Laboratory the initiative in key technical areas by combining the talents and efforts of our physical scientists and applied mathematicians. We concentrate on developing advanced N-body simulation techniques, including classical and quantum Monte Carlo techniques, molecular dynamics techniques, and

Langevin methods for stochastic differential equations. We also try to improve current algorithms used to simulate problems with disparate time and/or space scales.

This year we developed and applied a different algorithmic approach to the problem of quantum-mechanical simulations of hydrogen diffusing on and into the surface of a metal. Instead of performing a real-time simulation, we performed the simulation in imaginary time and then used Bayesian statistical inference methods to analytically continue the simulation data into real time. This method resulted in improved accuracy of predicted spectral properties of the diffusing hydrogen. Our most dramatic finding was a significant shift in vibrational frequencies from those predicted by normal-mode theory, underscoring both the quantum and the anharmonic nature of the hydrogen diffusion.

In addition, we developed a stochastic model of the bacterial flagellar molecular motor and applied our numerical methods to the direct simulation of stochastic differential equations.

Publications

Brandow, B., "The Exotic Superconductors: Characteristic Features and a Possible Explanation" (submitted to *Adv. Phys.*).

Castillo, J., et al., "A Generalized Length Strategy for Direct Optimization in Planar Grid-Generation" (submitted to *J. Comput. Phys.*).

Castillo, J., et al., "A Practical Guide to Direct Optimization for Planar Grid-Generation" (submitted to *SIAM Rev.*).

Davis, K., "PERs from Projections for Binding-Time Analysis," *J. Lisp Symbolic Comput.* **8**, 249 (1995).

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Adaptive Mesh Refinement Algorithm Development and Dissemination

Jeffrey S. Saltzman

Our objective is to develop and disseminate adaptive mesh refinement (AMR) algorithms for structured meshes. Areas of development include algorithms for parallel architectures, techniques for the solution of partial differential equations on adaptive meshes, mesh generation, and algorithms for nontraditional or generic applications of AMR. AMR algorithms are perceived as difficult to meld to current algorithms. Therefore, we are developing tools that diminish this perception and will allow more computational scientists to use AMR within their own work.

During this fiscal year, we have concentrated on developing algorithms that are conservative for adaptive overset grids. We have also supported some development work for an AMR library written in C++ called AMR++. This library is a collection of routines that facilitate the manipulation and generation of adaptive grids and data. Efforts for conservation include using both algebraic and Cartesian techniques to solve elliptic equations on overset adaptive meshes. Algebraic and Cartesian methods can possibly be extended to hyperbolic

and parabolic systems because the operator is cast in divergence gradient form. We have begun designing C++ sparse data structures that can be used not only for our methods but for any work that needs to be performed on data of codimension one.

Publications

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Neutron Transport Methods for 3-D Cartesian Adaptive Meshes

Raymond E. Alcouffe

The mesh representation of complex three-dimensional (3-D) geometries is currently accomplished using Cartesian grids that are very regular or arbitrary meshes that are accurate but do not have any regular connectivity. Methods that use regular grids are computationally efficient because the connectivity of the mesh is regular and well characterized. Arbitrary grids can accurately represent complex geometries, but the complex structure of the resulting matrices makes them difficult to solve efficiently. An efficient compromise is the adaptive Cartesian

mesh, which allows internal mesh refinement in areas where gradients in physical quantities (such as pressure, density, temperature, and neutron flux) are large. We are developing efficient numerical methods for the solution of the discrete-ordinates transport equation on such meshes.

Building upon the two-dimensional, adaptive-mesh solver that we developed last year, we have investigated 3-D solvers this year. The thrust of this development is to use parallel architecture in our 3-D calculations, and so we

have changed the focus of the effort in this direction. To formulate a 3-D, adaptive-mesh-refinement solver for the transport equation, we have gone to a more object-oriented paradigm, which is being done through FORTRAN90. Using the features of this language, we have explored the concept of solving the equations for the inversion of the transport operator cell by cell and in a block-of-cells method. Our results show that the cell-by-cell method as implemented on the Cray T3D is about a factor of 3 slower than our regular parallel sweeper. In going to the block sweeper, we hope to recoup much of the inefficiency of the cell-by-cell method in the parallel environment. We do not yet have results for the block-parallel sweeper.

Applications of Nonlinear and Stochastic Dynamics

Charles Doering

This project supported research in applications of nonlinear and stochastic dynamics systems with the aim of exploiting the last decade's progress in understanding the dynamics of nonlinear, or noisy, systems related to problems in theoretical physics, chemistry, and biology. The common denominator is the fundamental roles that nonlinearity, noise, and disorder play in the dynamics of both simple and complex systems. We also studied the underlying theoretical problems that have much in common within the paradigms of nonlinear science. The major areas of research included (1) stochastic models of molecular motors; (2) turbulent diffusion and convective heat transport; (3) self-

organized, spatial structures in nonequilibrium models; and (4) nonlinear wave and soliton applications in optics and ocean modeling.

Last year's accomplishments included (1) development of new, nonlinear, evolution equations for weakly nonlinear internal waves in a two-fluid system; (2) establishment of a framework for comparison of century-long simulations of the wind-driven double-gyre; (3) asymptotic solution of a model problem explaining the deflection of laser beams in plasma flows; (4) development of a scheme for stable pulse transmissions in optical fibers and investigation of the nonadiabatic dynamics of dark solitons; (5) demonstration of a

method for controlling front dynamics in reaction-diffusion systems with nonuniform external fields; and (6) derivation of rigorous bounds on heat transport by turbulent convection.

Publications

Cai, D., A.R. Bishop, and N. Gronbech-Jensen, "Discrete Lattice Effects on Breathers in a Spatially Linear Potential," *Phys. Rev. E* **53**, 1202-1205 (1996).

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Choi, W., and R. Camassa, "Long Internal Waves of Finite-Amplitude," *Phys. Rev. Lett.* **77**, 1759–1762 (1996).

Constantin, P., and C. Doering, "Heat-Transfer in Convective Turbulence," *Nonlinearity* **9**, 1049–1060 (1996).

Doering, C., et al., "Random Walks, Resonance, and Ratchets," in *Non-equilibrium Statistical Mechanics in One Dimension*, V. Privman, Ed. (Cambridge University Press, New York, 1996).

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Reimann, P., and T.C. Elston, "Karner's Rate for Thermal Plus Dichotomous Noise Applied to Ratchets," *Phys. Rev. Lett.* **77**, 5328–5331 (1996).

Salkola, M.I., A.R. Bishop, et al., "Coupled Spin-Boson Systems Far from Equilibrium," *Phys. Rev. B* **54** (18), 12645 (1996).

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Theoretical Foundation for Adaptive Monte Carlo

Richard Picard

The Monte Carlo method is a key tool for analysis of many complex problems, especially in the nuclear fields. This project is one of several that are aimed at significantly extending the effectiveness of the method.

The standard central limit theorem, applicable to Monte Carlo work where N simulation runs are statistically independent, provides for the standard deviation to converge to zero at the rate of the square root of N . Under restrictive conditions, the replacement of independent sampling with adaptive learning algorithms has recently been shown to provide exponential convergence. The goal of this project is to obtain exponential convergence under less restrictive conditions.

In the first year of the effort, we successfully generalized the existing theory, which required the simulation to visit all process states—a burdensome requirement for large problems.

We overcame this requirement through the use of interpolating smoothing functions. When the expected score conforms to a model linear in its parameters (such as a polynomial in several variables, for example), use of results from a full rank experimental design is sufficient to obtain exponential convergence. We discussed this work as part of an extensive workshop involving participants from across the international Monte Carlo community.

We also obtained simulation evidence of exponential convergence for Halton's sequential Monte Carlo method when applied to large, sparse matrices. Use of path information and splitting/roulette techniques accelerated this convergence.

In addition, our efforts in statistical mechanics focused on improving convergence properties of multi-canonical recursion algorithms, which overcome the long correlation times of the standard Metropolis algorithm.

Publications

Baggerly, K., "Part III: Interfacing Theory and Practice" (Adaptive Monte Carlo Methods, Los Alamos, N.Mex., August 14–16, 1996).

Cox, D., "Part II: Continuous State Spaces" (Adaptive Monte Carlo Methods, Los Alamos, N.Mex., August 14–16, 1996).

Kollman, C., K. Baggerly, D. Cox, and R. Picard, "Adaptive Importance Sampling on Discrete Markov Chains" (submitted to *Ann. Appl. Probability*).

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Advanced Three-Dimensional Eulerian Hydrodynamic Algorithm Development

William Rider

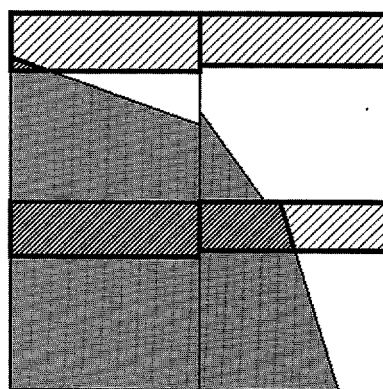
The purpose of this project is to investigate, implement, and evaluate algorithms that have high potential for improving the fidelity and efficiency of large-scale, three-dimensional, Eulerian hydrodynamic simulations. This project combines core strengths of several Laboratory divisions. The project is of high potential institutional benefit given the renewed emphasis on numerical simulations in science-based stockpile stewardship and the Accelerated Strategic Computing Initiative.

We used data generated in other projects, such as Telluride (a molding and casting simulation tool), as active platforms for testing our algorithms. Examples of algorithms we implemented are interface-tracking methods, multidimensional advection methods, interfacial physics, and parallel communication libraries.

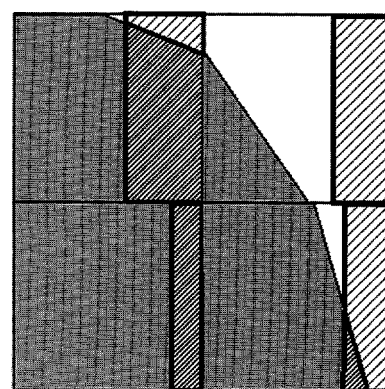
Chief among the improvements we made is the application of fully multidimensional methods for advection in the form of both interface-tracking and shock-capturing techniques. The first figure provides a graphical depiction of both standard and modified multidimensional interface-tracking methods. We found that these methods reduce the magnitude of grid-dependent effects and improve solution accuracy. These grid dependencies are most acute for converging coordinate frames.

Our implementation of interface tracking uses systematic techniques from computational geometry. The second and third figures show several fundamental aspects of this algorithmic approach.

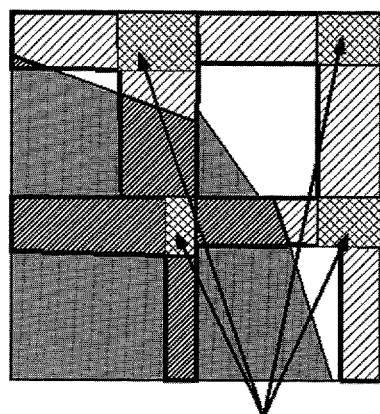
We achieved another important advance in interfacial closure of multifluid equations in both compressible and incompressible regimes by including relevant physical phenomena in a physical manner (the fourth figure shows two potential types of interface topologies).



(a) A y-direction pass of the operator split method.

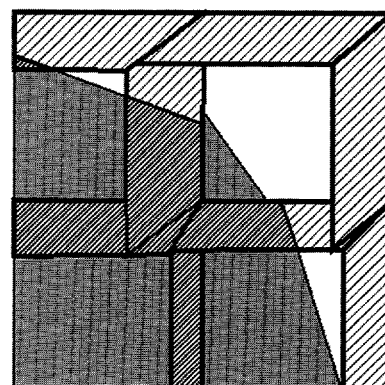


(b) An x-direction pass of the operator split method.



volumes fluxed twice

(c) The naive unsplit method.



(d) The unsplit method.

A comparison of three multidimensional advection schemes we investigated. For the operator split integration (a and b), the x-pass follows the y-pass. We do not recommend the naive unsplit method (c) because of its inability to advect volumes in a conservative, monotonic manner. We obtained the best results with the corner-coupled geometrically unsplit method (d).

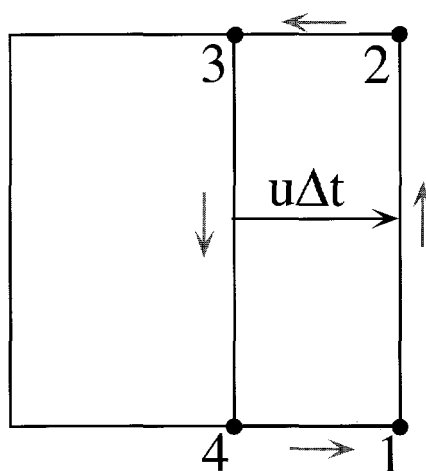
Publications

Rider, W.J., "Filtering Nonsolenoidal Modes in Numerical Solutions of Incompressible Flows" (submitted to *Int. J. Numer. Methods Fluids*).

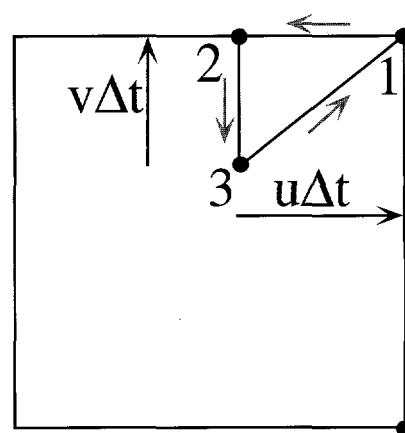
Rider, W.J., "Robust Formulation of Approximate Projection Methods for Incompressible Flows" (submitted to *J. Comput. Phys.*).

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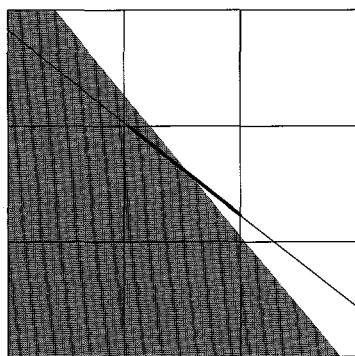
The method we implemented for computing the flux volume involves fundamental geometric steps (represented here as polygons). We formed these polygons by sweeping out areas with a positive velocity field.



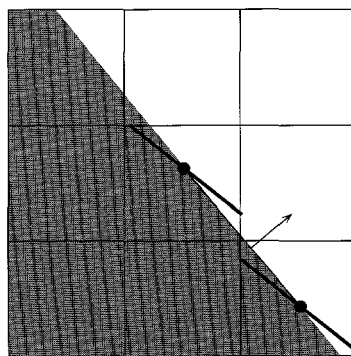
(a) Edge volume flux polygon.



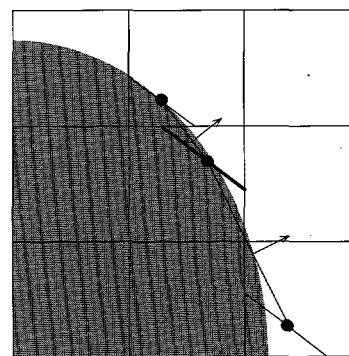
(b) Corner volume flux polygon.



(a) The initial normal and interface in the local stencil.

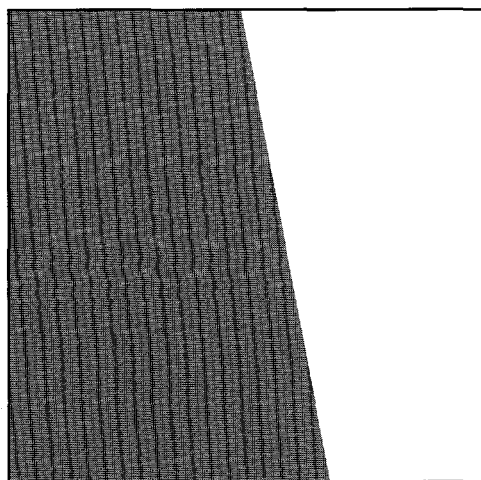


(b) A new guess at the normal.



(c) The method applied to a curved interface.

The interface reconstruction step is the function of several fundamental geometric steps.



(a) A simple unmixed cell.



(b) A complex well-mixed cell.

The algorithm for the interfacial physics treats unmixed or well-mixed cells self-consistently. This includes processes such as surface tension or solidification for low-speed casting applications or pressure and volume relaxation for high-speed hydrodynamics.

Phase Transitions, Nonequilibrium Dynamics, and Critical Behavior of Strongly Interacting Systems

Emil Mottola

In this project, we performed large-scale simulations of strongly interacting systems and investigated a variety of approaches to the nonequilibrium dynamics of phase transitions and critical behavior. Focus areas included (1) the finite-temperature, quantum chromodynamics (QCD) phase-transition and nonequilibrium dynamics of a new phase of matter (the quark-gluon plasma) above the critical temperature, (2) nonequilibrium dynamics of quantum fields using mean-field theory and, (3) stochastic classical field theoretic models with

applications to spinodal decomposition and structural phase transitions in a variety of systems such as spin chains and shape-memory alloys.

In FY 1996 we extended nonequilibrium field theory beyond mean-field techniques and studied rare B particle decays. We also performed a kink calculation for a sixth-order-polynomial strain-field theory that describes shape-memory alloys. Finally, we computed correlation functions, structure factors, and thermodynamic quantities like the specific heat for the alloys.

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Numerical Simulations of Disordered Superconductors

James Gubernatis

The objectives of this project included studying (1) the interplay of disorder and interactions in quantum systems with applications to mobility problems, the onset of superfluidity, disordered superconductors, and quantum phase transitions, (2) the problem of flux-line motion in superconducting materials with high critical currents, and (3) the development of software and computational algorithms for these classes of problems. Specifically, we carried out Monte Carlo studies of the critical behavior of superfluid ^4He in aerogel. We found that the superfluid density exponent increases in the presence of fractal disorder with a value roughly consistent with experimental results.

We also addressed the localization of flux lines caused by splayed columnar pins. Using a Sine-Gordon type of renormalization-group study, we obtained an analytic form for the critical temperature. We also determined the critical temperature from current-voltage characteristics obtained from a molecular dynamics simulation. The combined studies enabled us to construct the phase diagram as a function of interaction strength, temperature, and disorder.

Finally, we employed the recently developed mapping between boson world-lines and the flux motion in quantum Monte Carlo simulations to analyze localization in the presence of disorder. From measurements of the

transverse flux-line wandering, we determined the critical ratio of columnar-to-point disorder strength needed to localize the bosons.

Publications

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Transactional Memories: A New Abstraction for Parallel Programming

Joseph Fasel

Current distributed-memory multiprocessor computers make the development of parallel programs difficult. From a programmer's perspective, it would be most desirable if the underlying hardware and software could provide the programming abstraction commonly referred to as sequential consistency—a single address space and multiple threads. But enforcement of sequential consistency limits opportunities to optimize architectural and operating system performance and leads to poor performance. A new abstraction called “transactional memories” may provide a solution to this problem. The programming model is shared memory with multiple threads. However, we obtain data consistency through the use of transactions rather than mutual exclusion based on

locking. This transaction approach permits the underlying system to exploit the potential parallelism in transaction processing. We are exploring the feasibility of designing parallel programs using the transaction paradigm for data consistency and a barrier type of thread synchronization.

We experimented with alternative implementations of transactional memories, specifically a pessimistic approach, appropriate for low communication latency, and an optimistic approach for higher latency. The optimistic approach minimizes communication but increases the probability of a conflict being detected at transaction commitment. When such a conflict occurs, low-priority transactions may need to abort in favor of high-priority transactions. We improved on one

conflict-resolution scheme by establishing an order on conflicting transactions when a conflict is detected (called the “required commit order”). So long as this order is acyclic, no transaction need be aborted.

Unfortunately, our parallel virtual machine (PVM) implementation of transactional memory was not able to demonstrate a performance improvement over traditional approaches to parallel programming. As this situation probably results from PVM's high overhead and latency, we directed our efforts toward implementing a low-latency implementation of the message-passing interface (MPI is another standard parallel-programming library) on the Meiko CS/2 massively parallel super-computer and a cluster of workstations on a high-speed switch. We completed this implementation in the summer of 1996. At the end of FY 1996, we had not yet ported the transactional memory implementation to this new framework.

Development of an Integrated System for Estimating Human Error Probabilities and Modeling Their Effects

Heidi Hahn

This project is aimed at developing an expert system that will allow integrated error estimation using input from many different sources with differing quantitative bases. The resulting knowledge-based system will allow analysts to find appropriate human error probabilities (HEPs) for use in probabilistic risk assessment and human reliability analysis (HRA). Our system will (1) allow analysts to input relevant information; (2) compare the analyst's situation with different approaches and identify one or more “matches”; (3) provide valid estimates based on selected matches; and (4) provide an estimate drawn

from a weighted average across the matches, with weights being determined by the “goodness of fit” for each match.

So far, we have completed two tasks: we built a prototype system with limited data incorporated, and we validated system design with HRA practitioners. The prototype system now contains all but one of the major HRA methodologies used to generate HEPs. We will incorporate the remaining method, along with data from several minor sources, into the final system during the next project year.

We validated the initial system at a professional society meeting in September 1996. We guided HRA practitioners through a hands-on demonstration and had them complete a survey on system utility. We will use the data gathered at the meeting to guide further system development. Final validation will occur in the next phase of the project.

Publications

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Novel Monte Carlo Algorithms for Statistical Mechanics

James Gubernatis

The Monte Carlo method is a key tool for analysis of many complex problems. This project is aimed at significantly extending the effectiveness of the method and specifically looks at novel methods applicable to statistical mechanics.

We made progress on three problem areas. In the first, we successfully implemented the Gibbs ensemble method for a mixture of hard disks of vastly different radii. This implementation required devising special rules for moving large disks into regions of predominantly small disks, produced a much more efficient algorithm than the standard implementation, and permitted an extensive study of phase separation in mixtures.

In the second problem area, we developed a novel algorithm to simulate micelle formation in ternary fluid mixtures involving surfactants. The base system being simulated is an Ising model, and the new algorithm makes a special use of the Swendsen-Wang cluster algorithm to produce statistically independent configurations at each Monte Carlo step. With each new configuration, we used the inversely restricted sampling technique to grow the micelles. We computed micelle density and size distributions as a function of surfactant concentration.

For the third problem area, we studied in detail a collection of new algorithms to simulate first-order phase transitions, spin-glass problems, protein-folding problems, etc., that adaptively construct an importance sampling function. We identified three areas in which existing methods can be improved: the manner in which certain density functions are estimated, the manner in which the learning process is executed, and the manner in which the Monte Carlo samples the importance function. For the first area, we developed codes to permit the use of kernel estimation methods to improve the density function estimation. For the second, we identified several other learning processes that might be more effective and have started to test them. Work on the third area will occur in the coming year.

Advanced Computational Science

Andrew White

For this project we used advanced modeling and simulation techniques (both classical and learning-based) to try to predict the occurrence and course of various kinds of crisis events. Because of their complex, time-critical nature, these applications clearly emphasize the need for high-performance computing and communication technology.

Accurately predicting the course of wildfires (for example, in Yellowstone National Park and in Glenwood

Springs, Colorado) requires the integration of sophisticated turbulent burn models and adaptive mesoscale weather models. We have used a self-predicting transport description of the relevant combustion and transport phenomena to successfully characterize the bulk evolution of a wildfire. We then implemented this description in a computer code and validated it using data provided by the U.S. Forest Service.

Influenza is a prime example of a reemergent viral health threat, and it is a prototype for threats from natural and artificial biological agents. We are working with the Center for Disease Control (CDC) to define and

implement a unique database that will provide researchers with validated influenza sequence data. We have developed a model of influenza epidemiology that includes the implementation of antiviral drug treatment and the possibility that the virus will be drug resistant.

Unusual periods of excessive heat can lead to increased mortality. For example, from July 11 to July 27, 1996, Chicago, Illinois, recorded 465 heat-related deaths. We are studying improvements to the "effective temperature" index (comprising temperature and humidity) that is commonly used. To that end, we are studying historical weather data (1973–1993) from the National Oceanographic and Atmospheric Administration (NOAA) and mortality data from the CDC through the use of Expert Network modeling tools that combine the best features of rule-based systems and neural networks.

Development of an Automated Core Model for Nuclear Reactors

Russell Mosteller

This project is aimed at developing an automated package of codes that can model the steady-state behavior of nuclear-reactor cores of various designs. As an added benefit, the data produced by the steady-state analysis can also be used as input to the TRAC transient-analysis code for subsequent safety analysis of the reactor at any point in its operating lifetime.

The basic capability to perform steady-state reactor-core analysis already exists in the combination of the HELIOS lattice-physics code and the NESTLE core-simulation code. Our purpose is to complete the automated package by obtaining cross-section libraries for HELIOS,

developing a linkage code to transform HELIOS output into NESTLE input, developing additional steady-state thermal-hydraulics modules for NESTLE, and benchmarking HELIOS and NESTLE both individually and in combination.

During this reporting period, we have completed the standalone benchmarking of NESTLE and performed extensive benchmarking of HELIOS. We have also obtained a new version of HELIOS, along with several new cross-section libraries for it. These new libraries are based on ENDF/B-VI Release 3, whereas the old libraries were based on ENDF/B-VI Release 2. Currently, we are

benchmarking HELIOS with the new libraries, a task we previously performed with the old libraries. Finally, we also began writing the linkage code that will transform HELIOS output into NESTLE input. Completing that linkage code will be the next step in our project.

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Density Function Estimation for Monte Carlo Simulations

James Gubernatis

Applying modern statistical methods to experimental data can dramatically enhance the information extracted, effectively increasing the efficiency of data collection. Most modern statistical methods for estimating density functions begin with histograms as a crude estimate and then move on to a wide variety of more sophisticated and powerful methods such as kernel estimators, orthogonal series, and maximum penalized likelihood methods.

The goal of this project is to use modern statistical methods, such as advanced density function techniques, to analyze Monte Carlo data. Specifically, we are adapting such methods to determine the configurational

densities of states in order to evaluate the free energies in phase equilibria. This is a long-standing problem in the application of the Monte Carlo method.

Presently, density function estimation is a key step in the Swendsen-Ferrenberg histogram method for postsimulation data analysis and in adaptively improving the importance sampling in recently proposed methods such as multicanonical and simulated tempering algorithms. In each case, a simple histogram method is used to estimate the density

function. For the postsimulation analysis, we showed that although advanced kernel estimation methods can improve the representation of the density function, there is little advantage to using an estimator other than a histogram because the estimate is subsequently used to compute average quantities. We are presently investigating the use of these advanced methods to adaptively construct the importance sampling function used in simulations. Here we expect these new methods to offer a significant advantage.

Self-Organization and Pattern Formation

Robert Ecke

The formation of regular structures is important in science and technology, and recently there has been much attention focused on self-organizing and self-assembling systems. Instead of building structures by hand, as in microelectronic lithography, one would design or search for systems that put themselves together. If successfully developed, self-organizing and self-assembling systems could have a major impact on a wide range of technologically useful applications.

One variety of such systems is pattern-forming systems that can produce simple regular and irregular structures. Two examples of pattern formation are thermal convection and reaction-diffusion systems, in which two-dimensional patterns of stripes, spirals, targets, hexagons, squares, and "self-replicating" spots have been observed and modeled. The elucidation of types of patterns, their dynamics, and the possible application of such mechanisms to problems of technological interest is a large part of our work. Specific systems we have studied are spatio-temporal patterns in cellular automata, defects in rotating thermal convection (shown in accompanying figure), replicating spot dynamics in reaction-diffusion systems, and spatio-temporal dynamics of

calcium waves (as models of biological self-organization).

Our successes include demonstrating the nucleation mechanism for dislocations with rotation and measuring the long-wavelength distortion angle. We have also extended the study of multivalued front speeds to the derivation of dynamical equations for front transitions and correctly predicted spontaneous transitions between counterpropagating fronts. We have further suggested a way to control domain patterns using a spatially nonuniform, external advective field. In the simulation area, we have written a three-dimensional simulation code for message-passing machines such as the T3D machine to elucidate the role of various cell processes for Ca^{2+} dynamics. We also demonstrated numerically and analytically that a self-organization process is intrinsic to the dynamics of microtubules.

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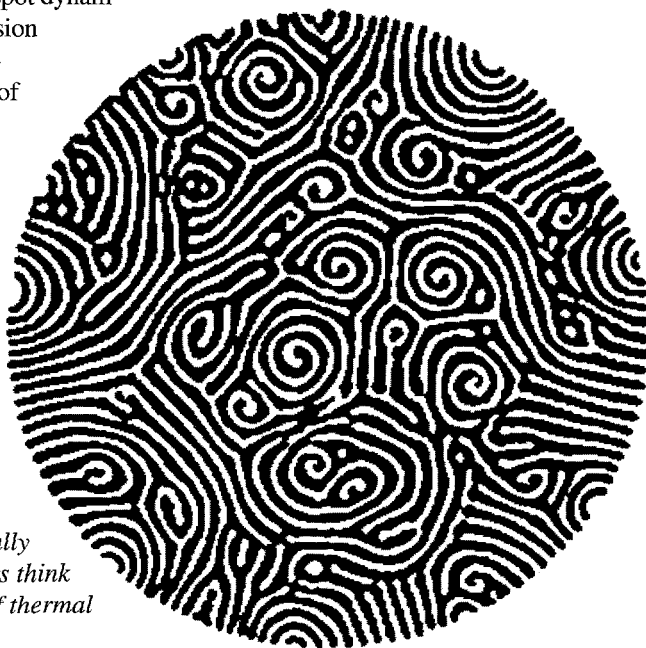
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Application of Discrete Mathematics

Vance Faber

This project in combinatorial analysis is aimed at studying and quantifying the properties of discrete objects and their operations. The knowledge gained is applicable to all areas of science and engineering. Our goal is to extend the combinatorial method as a viable and useful tool to help in solving Laboratory problems. Since this project was conceived, we have used the methods of combinatorics to solve problems in numerical analysis, computer networks, cluster analysis, learning theory, DNA mapping, group testing for biology, evolutionary trees, quantum physics, and wavelet analysis. The basic approach of the researchers participating in this project is to gain a deep understanding of problems arising in laboratory research and to use their skills in combinatorial methods to solve them.

In the field of quantum computing, we have designed several new and efficient algorithms for quantum error correction and fault-tolerant computing. As a result of this and other work, quantum computing has been proven to be physically realizable. In communication networks we have developed new approximation algorithms for several basic problems that arise in network design and analysis. These algorithms will potentially be useful in upgrading network performance and especially in finding efficient routing methods.

In computational finance we have applied innovative computational methods to pricing various derivatives and options. In computational geometry we have found efficient methods for point location and Delaunay triangulations as well as efficient computational methods for geometric problems arising in pattern matching and cartography. We continue to develop methods for efficient cluster analysis. The algorithms, some of which have been patented, are now being extensively used at the Laboratory.

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Theory and Modeling of Correlated-Electron Materials

Alan Bishop

There is today a significant opportunity for exploiting complex electronic materials based on properties totally beyond those of traditional solid-state materials. The new materials are characterized by strong competitions between coupled electronic, structural, and magnetic degrees of freedom and by sensitivities to dimensionality and geometry. This project provides theory and modeling of correlated electronic materials for three major tasks:

(1) isolation of novel phenomena; (2) integration of synthesis and characterization with theoretical modeling of phenomena in specific classes of materials; and (3) development of scientific control of synthesis-microstructure-property relationships. These tasks in turn address three critical science issues at the cutting edge of research in correlated electronic materials: What are the roles of electron-electron and electron-lattice interactions, disorder, chemical doping, magnetic field, pressure, and temperature in controlling metal-insulator transitions? What conditions induce non-Fermi-liquid metallic behavior and what are their experimental signatures? How can the local structure of these materials be probed?

We have worked closely with experimentalists to study the origin and detection of intrinsic fine-scale structure in strongly correlated electronic materials, including double-exchange and Jahn-Teller effects in perovskite oxides, that leads to the polaronic and elastic short-range textures recently observed through neutron, x-ray, and resonant ultrasound probes. We have begun pair-distribution function analysis of models with local and long-range order. We have developed new nonperturbative methods for, and increased our understanding of,

nonadiabatic and inelastic quantum transport, including multiple spatial- and temporal-scale effects. We have modeled the origins of non-Fermi-liquid and pseudogap behavior in perovskites and heavy-fermion compounds, including intrinsic and extrinsic disorder, d-wave symmetries, and multiphonon bound states. Finally, we have established regular discussion and seminar sessions for communication between and among experimentalists and theorists.

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Geoscience, Space Science, and Astrophysics

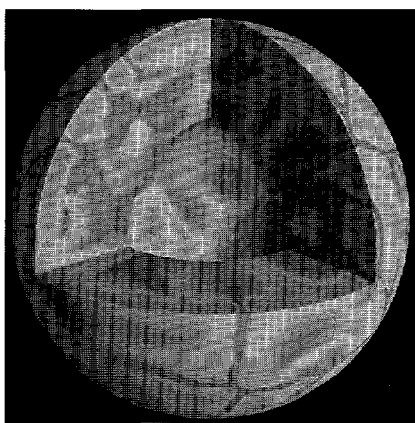
Modeling the Heat Flow and Resulting Dynamics in Earth's Interior

Gary Glatzmaier

We have used computer simulations and laboratory experiments to study the dynamics of Earth's deep interior. Our computer models have simulated the flow in Earth's mantle on relatively small scales such as within magma chambers, below volcanoes, and beneath midocean ridges. These three-dimensional models of localized features have demonstrated the effects of the highly temperature-dependent viscosity of mantle material on the structure of the fluid flow and on the transport and mixing of different minerals within the mantle.

Our global three-dimensional models of mantle convection have also uncovered how sensitive the global-scale flow structure is to the variation of the viscosity throughout the mantle. In particular, we have found that it is very likely that the lower part of Earth's mantle has a much higher viscosity than the upper part; our simulations that have this same variation in viscosity produce subduction-like downflows at the surface that are very much like those seen on Earth at the boundaries between tectonic plates (see accompanying figure).

We have also conducted several laboratory experiments of convection in viscous fluids to complement our computer modeling studies and provide further insight into convective mixing. In addition, we are using geochemical observations of Earth to constrain the dynamics of our computer models by estimating the amount of mixing that has occurred in Earth's mantle.



A snapshot of our global simulation of convection in Earth's mantle. The image shows cold (dense) material as a dark shade and warm (buoyant) material as a light shade. A cutaway of the mantle shows the structure down to the core. The long and narrow dark regions on the surface resemble subduction zones on Earth.

Publications

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Kincaid, C., G. Ito, and C.W. Gable, "Laboratory Investigation of the Interaction of Off-Axis Mantle Plumes," *Nature* **376**, 758 (1995).

Kincaid, C., J.-G. Schilling, and C.W. Gable, "The Dynamics of Off-Axis Plume-Ridge Interaction in the Uppermost Mantle," *Earth Planet. Sci. Lett.* **137**, 29 (1996).

Olson, P., and G.A. Glatzmaier, "Magnetosconvection in a Rotating Spherical Shell: Structure of Flow in the Outer Core," *Phys. Earth Planet. Inter.* **92**, 109 (1995).

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Remote Sensing Science Thrust: New Concepts

Siegfried Gerstl

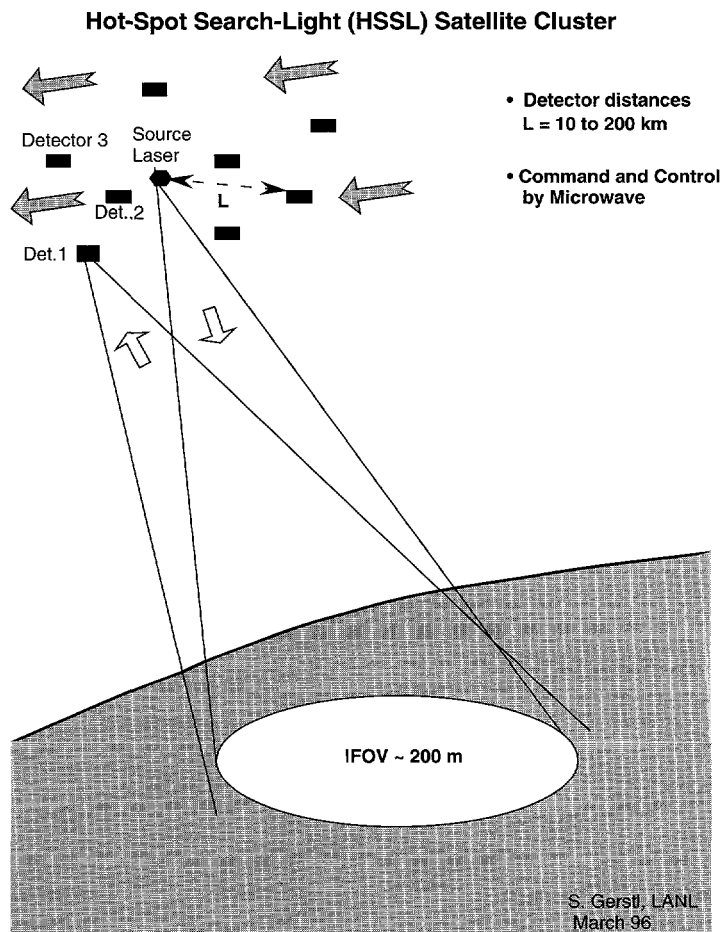
The primary objective of this project is to evaluate the feasibility of new research ideas that are based on extrapolations of science and technology that are already at the forefront of remote sensing science. These studies have provided timely input for NASA's future civilian research, the New Millennium Program, and the U.S. Air Force Scientific Advisory Board.

We have looked at a promising concept for measuring vegetation canopy hot-spot characteristics from space. The concept involves active illumination and bistatic detection that would allow angular distribution measurements from space in a searchlight mode, which is equivalent to measuring a localized bidirectional reflectance distribution function (BRDF). The concept comprises a pointable illumination source, such as a laser operating at an atmospheric-window wavelength, coupled with a number of high-spatial-resolution detectors (clustered around the illumination source in space) that receive photons nearly coaxial with the retroreflection direction. Microwave control and command among the satellite cluster would allow simultaneous orientation of the direction of the laser beam and the telescope detectors so that the coupled system can function like a searchlight with almost unlimited pointing capabilities. The concept is called the hot-spot search-light (HSSL) satellite cluster and is shown in the first figure. A nominal altitude of 600 km for the satellite cluster will allow hot-spot BRDF measurements out to about an 18-deg phase angle.

We have also demonstrated the feasibility of an environmental volumetric imaging (EnVI) concept that would use active remote sensing from space to measure the distribution and density of foliage in a vegetation

canopy. Our model simulations and information retrieval algorithms show that EnVI cannot only measure the total leaf area index (LAI) but also the vertical distribution of the LAI. The second figure shows the results of

simulated remote measurements of a canopy from 10-km altitude on two different vertical leaf distributions with the same leaf area index. Based on these encouraging results, we are initiating collaborations with experts outside Los Alamos to develop laser remote sensing altimeters.



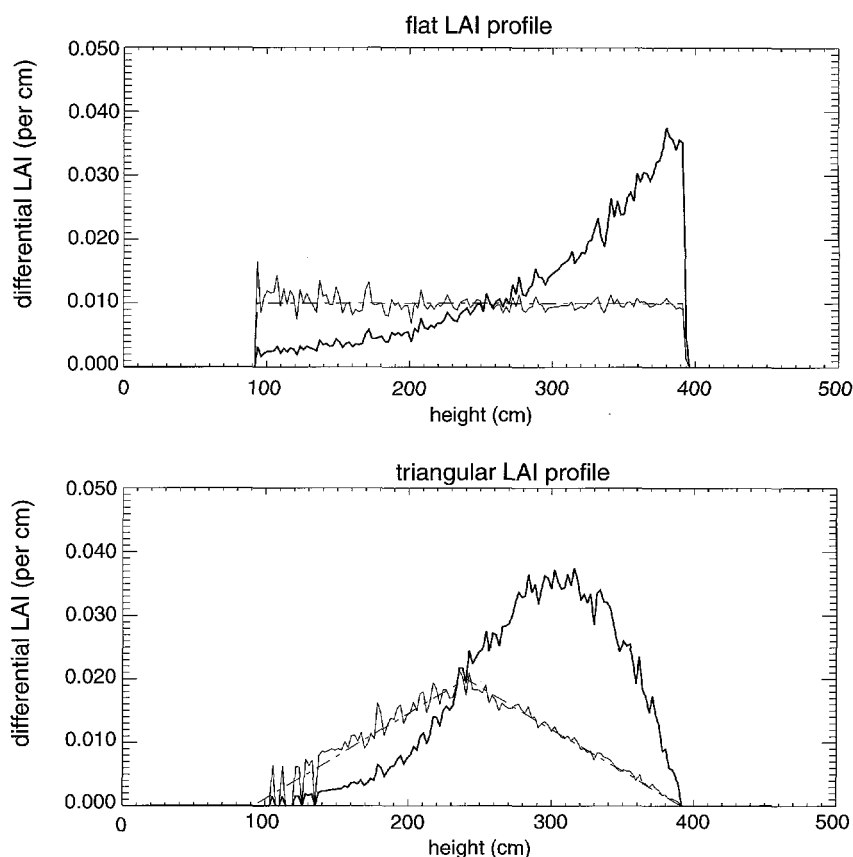
The hot-spot search-light satellite concept, a free-flying constellation of a central laser source and a surrounding cluster of detector telescopes at distances of 10 to 200 km from the source, for an instantaneous field-of-view (IFOV) of 200 m.

Publications

Gerstl, S.A.W., "Angular Signatures, and a Space-borne Measurement Concept," *IGARRS'96 Symp. Proc.* **3**, 1642 (1996).

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Simulated measurements of vertical leaf area index (LAI) distribution profiles with the environmental volumetric imaging (EnVI) concept. The leaves are distributed uniformly over 3 m in the top panel and in a triangular distribution shape in the lower panel. The thick lines show the timing profile of the singly reflected laser photons. The thin solid lines are the differential LAI distribution as derived from the photon counting; these match well with the input differential LAIs.

Subsurface Noble Gas Transport at the Nevada Test Site

Joseph Thompson

The objectives of our research are to explain the results of a groundwater pumping test done from 1975 to 1991 at the location of the nuclear test Cambric at the Nevada Test Site and, especially, to examine and understand the subsurface transport of noble gas. The elution data from the pumped well showed that the appearance of krypton in the elution was delayed relative to tritium and that only half of the calculated Kr-85 source term was ever removed. We hypothesized that carbon dioxide gas that evolved from

the carbonate rock around the nuclear device contributed to the post-detonation migration of Kr-85 throughout the rubble chimney above the collapsed crater. The distribution of krypton was thus different from that of tritium, which was contained in the immediate vicinity of the cavity. This initial distribution of krypton resulted in some losses of Kr-85 from the groundwater and in its delayed arrival, relative to tritium, at the pumped well.

Our major accomplishment this year was to develop a three-dimensional model using the Los Alamos TRACR3D code that simulates the movement of tritium and krypton through the groundwater as it moves to the pumped well at the Cambric site. The model showed that the delayed arrival and loss of krypton could indeed be explained but that there was substantial uncertainty about initial radionuclide distribution, hydrologic parameters, and other factors. In addition, we began to consider the influence of thermally induced convection currents on the distribution of radionuclides around the location of the nuclear test. We are using the TRACR3D code to simulate buoyancy-driven flow to determine its significance in the Cambric study.

Analysis and Visualization of Global Magnetospheric Processes

Dan Winske

The purpose of this project is to develop new computational and visualization tools to analyze particle dynamics in Earth's magnetosphere. These tools will allow us to construct an efficient global picture of particle fluxes that requires only a small number of satellite measurements as input parameters.

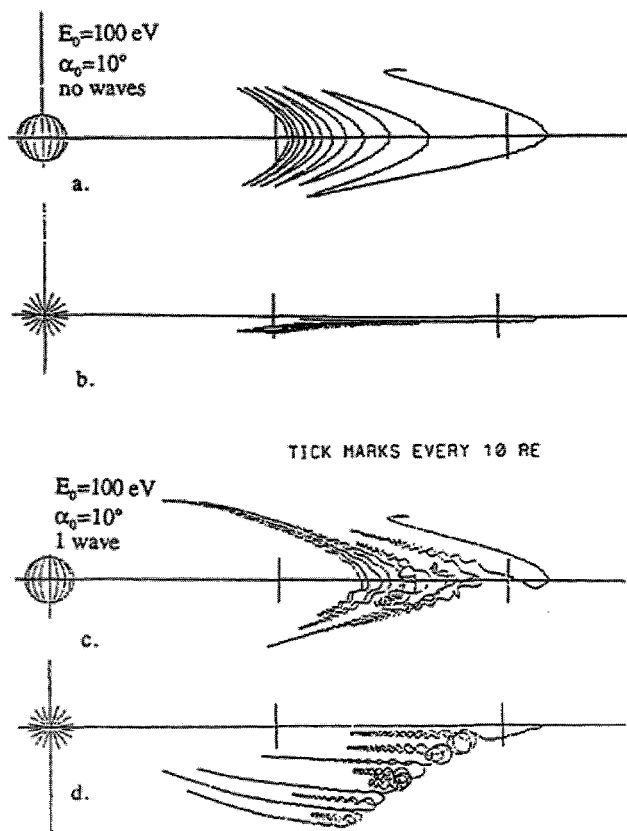
The visualization tools developed have led to a better understanding of particle dynamics in Earth's magnetotail in the presence of turbulent wave fields (see first figure). They have also demonstrated how large electromagnetic pulses in the solar wind can interact with the magnetosphere to increase the population of energetic particles and even form new radiation belts (see second figure). The work performed in this project has application to auroral, ionospheric, and magnetospheric phenomena, to plasma kinetics, transport, and impurities, and to plasma waves, oscillations, and instabilities.

Publications

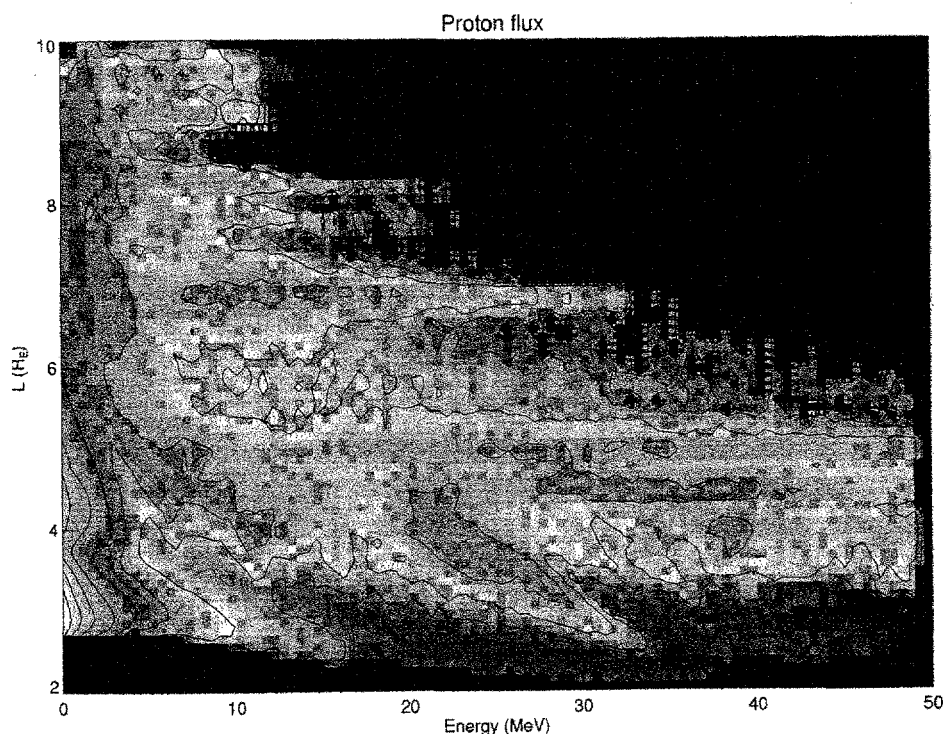
Cattell, C., I. Roth, and M. Linton, "Effects of Low-Frequency Waves on Ion Trajectories in the Magnetotail," *Geophys. Res. Lett.* **23**, 3445 (1995).

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Effect of a turbulent wave on the trajectory of a 100-eV proton with an initial pitch angle of 10° in the magnetotail. The upper two plots show the proton's trajectory in the absence of turbulence in (a) the x-z and (b) x-y planes (x corresponds to the sun-Earth direction and is the horizontal axis in each panel, z points to the north, and y is the cross-tail direction). The small figures to the left show the orientation of the magnetic field. In these two plots, the proton's motion is essentially adiabatic, combining gyration, bounce, and magnetic-field-gradient drift motion. The lower two plots show how a single monochromatic wave with an amplitude of 10 mV/m affects the proton's trajectory: the proton is (c) chaotically scattered in the current sheet region (near $z = 0$) and (d) drifts much farther in the direction of the cross-tail electric field, increasing its energy.



Calculation of the proton flux that results from a large solar wind storm. The plot shows the flux intensity (white is most intense, dark is less intense) as a function of energy and of the L shell (a ratio given in Earth radii). Such plots can be compared with data obtained directly from spacecraft, such as NASA's CRRES satellite.

Neutron Star Evolution and Emission

Richard Epstein

We have studied the physics of compact stellar objects. Our research has focused on three areas: the internal dynamics of neutron stars, their interactions with other stars, and the development of new techniques for observing them. The first focus of our research has been the anomalous behavior of pulsars—spinning, strongly magnetized neutron stars. We found that the observed sudden changes in the star's spin rate, so-called "glitches," may be due to cracking of the star's hard crust that produces heat, thereby altering the spin rate of the star's superfluid interior. Additionally, we found that the star's behavior after a glitch reveals that the crust and liquid interior are threaded by a magnetic field of at least a trillion gauss.

The second focus was the interactions among stars in crowded regions of galaxies, such as near galactic centers. We discovered that high-velocity collisions between red-giant stars and compact objects led to significant mass loss. These results appear to explain the puzzling dearth of red supergiants near the center of our galaxy and may provide an explanation for the source of mass that falls into the massive black holes in quasars.

The third focus was the development of a laser-powered cryogenic cooler for spaceborne astronomical observations. Such reliable and long-lived devices would facilitate sensitive gamma-ray spectral observations of gravitationally shifted nuclear lines from the surface of neutron stars.

Publications

Abney, M., and R.I. Epstein, "Ekman Pumping in Astrophysical Bodies," *J. Fluid Mech.* **312**, 327 (1996).

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Link, B., and R.I. Epstein, "Thermally-Driven Neutron Star Glitches," *Astrophys. J.* **457**, 844 (1996).

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Remote Sensing Science Thrust: Laser Remote Sensing

Siegfried Gerstl

The focus of our work is to extend a Raman lidar system to the measurement of atmospheric constituents such as aerosols and water vapor with unprecedented accuracy and range resolution. This work will be applied to non-proliferation and environmental boundary-layer science. Upgrades to the system included the addition of a line-narrowed Nd:YAG laser for temperature measurements and improving the command and control software. To understand the measurements, we are developing a microscale boundary-layer model with 2-m resolution. We fielded the upgraded lidar system in a central Pacific experiment, and we are using the data to validate the high-resolution microscale boundary-layer model.

In March 1996, we used the advanced scanning Raman lidar to quantify processes associated with the ocean-atmosphere interface, including intermittency and coherent atmospheric features in the "warm pool" of the tropical western Pacific near Manus Island. The data shows excellent vertical and horizontal, microscale spatial and temporal structure in the equatorial Marine Atmospheric Boundary Layer (MABL). The data included, for the first time, an observation of microscale cellular convective structures with hexagonal patterns associated with Rayleigh-Benard-like cells (see the accompanying figure).

To characterize the structures involved with the mass-energy exchange at the ocean-atmosphere interface, we used the scanning Raman lidar to image the three-dimensional structures found in the surface layer of the MABL. Although the atmospheric boundary layer is turbulent on small

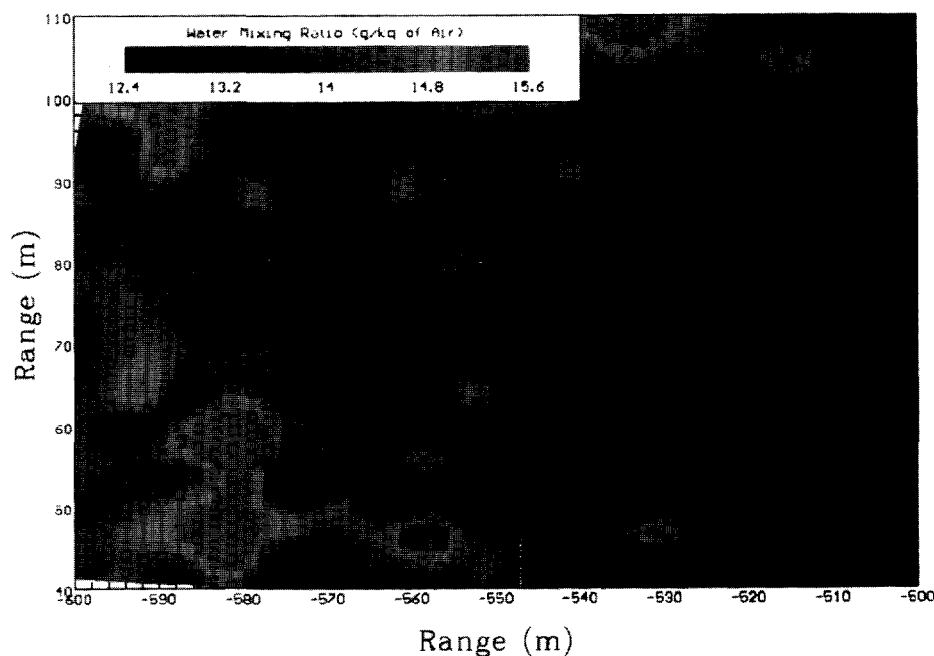
length scales, the large-scale structure may have length and time scales similar to those from linear stability analysis of thermal convection in a bounded thermal layer. Analysis suggests that the large-scale motions of the equatorial MABL are consistent with weakly turbulent, small-scale Rayleigh-Benard-like convective processes. To address these important issues, we will perform future lidar experiments capable of resolving the temporal behavior of the equatorial MABL.

In a further complementary effort, we developed an innovative method for determining water-vapor-column irregularities by microwave interferometry. This new method exploits archival radioastronomical data from the Very Large Array.

Publications

Cooper, D., W. Eichinger, R. Ecke, et al., "Initial Investigations of Micro-Scale Cellular Convection in an Equatorial Marine Boundary Layer Revealed by Lidar," *Geophys. Res. Lett.* **25** (1), 45 (1997).

Jacobson, A.R., and R. Sramek, "A Method for Improved Microwave-Interferometer Remote Sensing of Convective-Boundary-Layer-Turbulence, Using Water Vapor as a Passive Tracer" (to be published in *Radio Sci.*).



A horizontal Raman lidar scan of water vapor acquired 10 m above the ocean surface on March 26, 1996, in the tropical western Pacific near Manus Island.

Development of the First Nonhydrostatic, Nested-Grid, Grid-Point Global Atmospheric Modeling System on Parallel Machines

Chih-Yue J. Kao

All of the existing global atmospheric models suffer from one or more of the following shortcomings: (1) lack of an interactive nested-grid capability, which makes it difficult to evaluate the regional impact; (2) spherical spectral representation (as opposed to grid-point finite-difference) of model variables, which hinders model performance on parallel machines; and (3) use of the hydrostatic approximation, which makes the models potentially ill-posed. As a result, no atmospheric model is capable of simulating the full range of spatial scales of atmospheric circulations from global-scale wave disturbances to microscale plume dispersion.

The goal of this work is to develop a nested-grid, global atmospheric

modeling system (GAMS) with state-of-the-science physics and chemistry. This highly modularized, self-calibratable system will also provide a unique testbed for high-performance computing architecture.

We have successfully tested a global reduced-grid system in GAMS and the lower boundary conditions in terms of sea surface temperature and orography in the model. We have also studied the intrinsic difference between the hydrostatic and non-hydrostatic global models and are preparing a manuscript on this work. We have tested many three-dimensional elliptical equation solvers to find a fast convergence rate of the pressure solution and decided to use the Conjugate Gradient method.

Our prototype model runs on a wide range of computer platforms, includ-

ing an IBM R-6000 workstation, a Cray Y-MP, and a highly parallel CM-5. All of the necessary physical algorithms have been developed, including cloud and radiation parameterizations, boundary layer treatment, and a soil module.

Publications

Kao, C.-Y.J., A. Quintanar, M.J. Newman, et al., "Climate Simulations with NCAR CCM2 Forced by Global Sea Surface Temperature in 1950–1989," *J. Climate* **9**, No. 12 (1996).

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Smith, W.S., and C.-Y.J. Kao, "Stratocumulus-Capped Boundary Layer and its Diurnal Variation," *Monthly Weather Review* **8**, 1803–1816 (1996).

Production and Application of High-Specific-Activity Si-32

Dennis R. Phillips

In this project we have worked to produce the radionuclide Si-32 with unusually high specific activity and to develop methods for using Si-32 in oceanographic field research on factors affecting the global climate.

In collaboration with researchers from the University of California at Santa Barbara, we developed biological oceanographic experiments using Si-32 as a tracer to measure silicate uptake by diatoms, siliceous phytoplankton that require silicate as a nutrient. Because of their sheer volume, the diatoms sequester significant amounts of atmospheric

carbon dioxide. By correlating the data from our silicate-uptake studies with data from studies on the uptake of other essential nutrients, such as bicarbonate, inorganic nitrogen, and inorganic phosphorus, we can provide important information on the role of diatoms in the global climate. Furthermore, current theories indicate that silicate may be the limiting nutrient in some important ocean bodies, and our data from this project can be used to test such models.

This year we refined our radio-analytical techniques, focusing on calibration methods. After validating

the calibration methods, we analyzed data collected during the 1995 Coastal Ocean Processes research cruise in Monterey Bay (sponsored in part by the National Science Foundation and the Monterey Bay Aquatic Research Institute). We completed and submitted for publication two papers that describe the methods and the results of our experiments.

Publications

Brzezinski, M.A., and D.R. Phillips, "Evaluation of Si-32 as a Tracer for Measuring Silica Production Rates in Marine Waters" (to be published in *Limnology and Oceanography*).

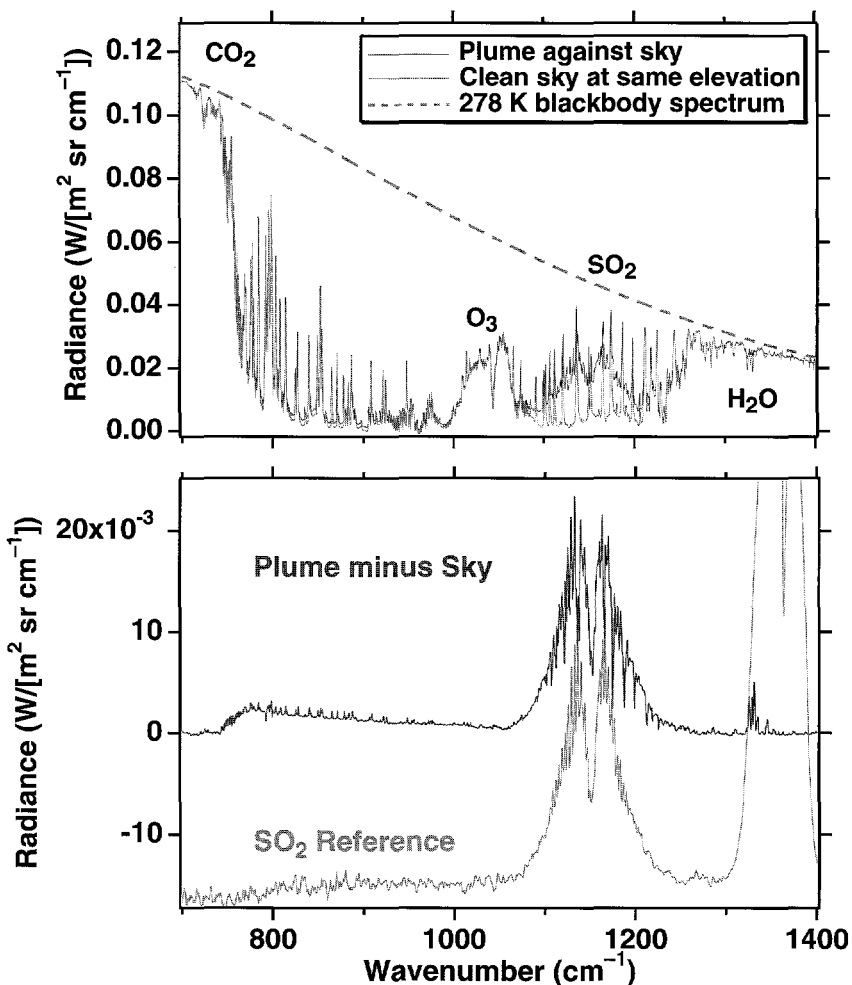
Brzezinski, M.A., and D.R. Phillips, "Silica Production in the Monterey, California, Upwelling System" (submitted to *Limnology and Oceanography*).

Remote Sensing Science Thrust: Hyperspectral Sensing

Siegfried Gerstl

Our goal is to develop detector technologies using hundreds of narrow spectral bands for remote sensing. We are concentrating on the infrared portion of the solar spectrum at hyperspectral resolution. We have made proof-of-concept measurements with a modified Fourier transform infrared (FTIR) spectrometer, identifying gaseous species in plumes from passively degassing volcanoes. We used a combination of (1) passive remote sensing with the FTIR spectrometer for multiple species concentrations and/or ratios and (2) active remote sensing with the elastic lidar data to remotely quantify (10% error) plume species fluxes. We are using these methods in parallel with traditional COSPEC, a correlation spectrometer operating in the solar ultraviolet (for SO_2 flux), and direct sampling methods (for total chemical composition) to obtain ground-truth measurements of the new techniques. We successfully field-tested these techniques at the White Island and Ruapehu volcanoes in New Zealand.

We detected the White Island plume at a distance of 50 km and made routine measurements at 6 km from Ruapehu. We easily identified both H_2O and SO_2 in the plumes of both volcanoes from distances up to 6 km. The first figure shows the SO_2 and H_2O spectra obtained at Ruapehu. While the standard HgCdTe detector provides optimum performance in the long-wave infrared region (8–12 μm), the addition of an InSb detector allowed us to obtain high-quality spectra in the 3–5 μm region, thus permitting the detection of HCl in the White Island plume from a distance of 1 km (see the second figure). All FTIR measurements were completely passive, i.e., they did not rely on artificial infrared sources or



Passive FTIR spectra of the Mt. Ruapehu plume on May 10, 1996, obtained from a distance of 6 km. (Top) Radiometrically calibrated long-wave infrared spectrum of the volcanic plume viewed against clear sky (heavy line) compared with a spectrum of a segment of sky at the same elevation angle but without any plume (fine line). For reference, the dashed line shows a blackbody spectrum at the ambient air temperature of 278 K. The most prominent divergence of the two spectra, the broad double-peaked feature extending from 1100 to 1200 cm^{-1} (9 to 8.3 μm), is due to SO_2 in the plume. The bottom figure shows the difference between the two spectra in the top figure. The many sharp lines throughout the 800–1000 cm^{-1} region are due to water vapor.

known emissions of radiation from hot rocks or lava. Our detection and quantification of volcanic HCl by completely passive means is a first and opens up a much greater range of volcanoes for study.

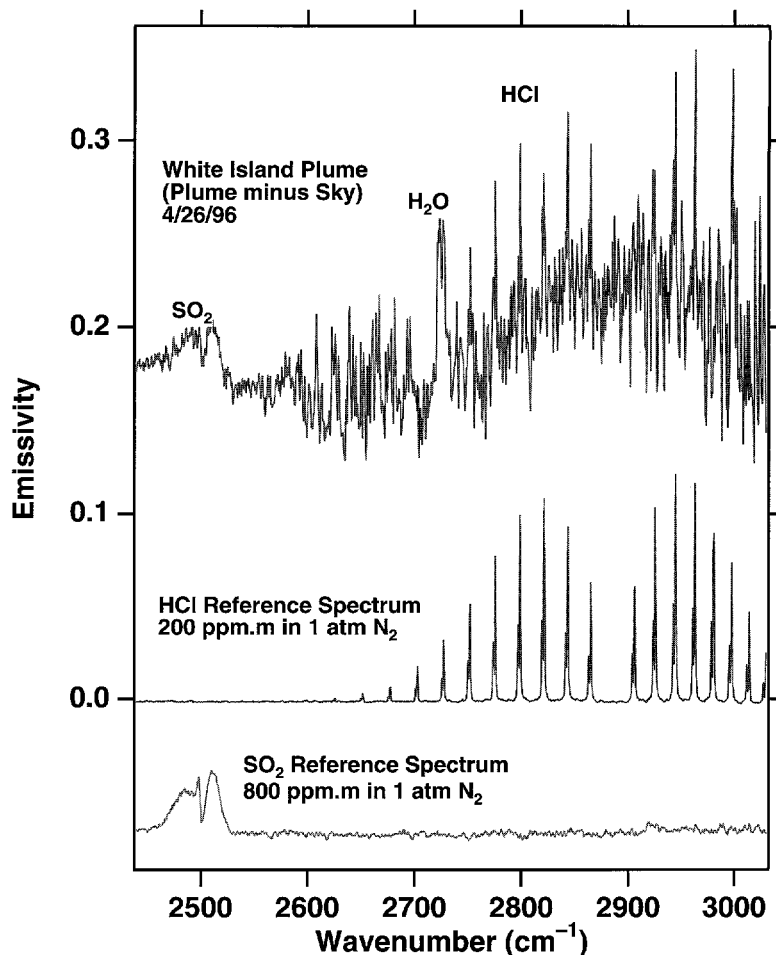
The incorporation of absolute radiometric calibration by means of specially constructed, portable, blackbody reference sources is another first performed in our project. Radiometrically calibrated measurements, combined with simultaneous COSPEC measurements of SO₂ path densities, allow plume temperature measurement. This, in turn, allows accurate determination of the concentrations of the other gases from the infrared spectra. We found SO₂/H₂O ratios determined in this manner to be in good agreement with those obtained from direct sampling of the fumerole gases.

Publications

Christenson, B., J. Lindsay, F. Goff, et al., "Direct Sampling and COSPEC Results Supporting FTIR and LIDAR Measurements of Volcanic Emission at White Island and Ruapehu Volcanoes," *EOS Trans. Amer. Geophys. Union* **77**, F830 (1996).

Cottingame, W., D. Pettit, S. Love, et al., "Integrated LIDAR/UV/IR Remote Sensing of Volcanic Emissions at White Island and Mt. Ruapehu, New Zealand," *EOS Trans. Amer. Geophys. Union* **77**, F801 (1996).

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Passive FTIR of the White Island plume, midwave infrared region, illustrating the first completely passive quantification of the ratio of HCl to SO₂ in a volcanic plume. Upper curve shows the plume-sky difference, as in the first figure, converted to emissivity using an estimated plume temperature of 310 K. The lower two curves show laboratory reference spectra of HCl and SO₂. Both the broad SO₂ feature and the regularly spaced sharp lines of HCl are clearly evident in the plume spectrum.

Studies of Dynamical Processes Affecting Global Climate

Charles Keller

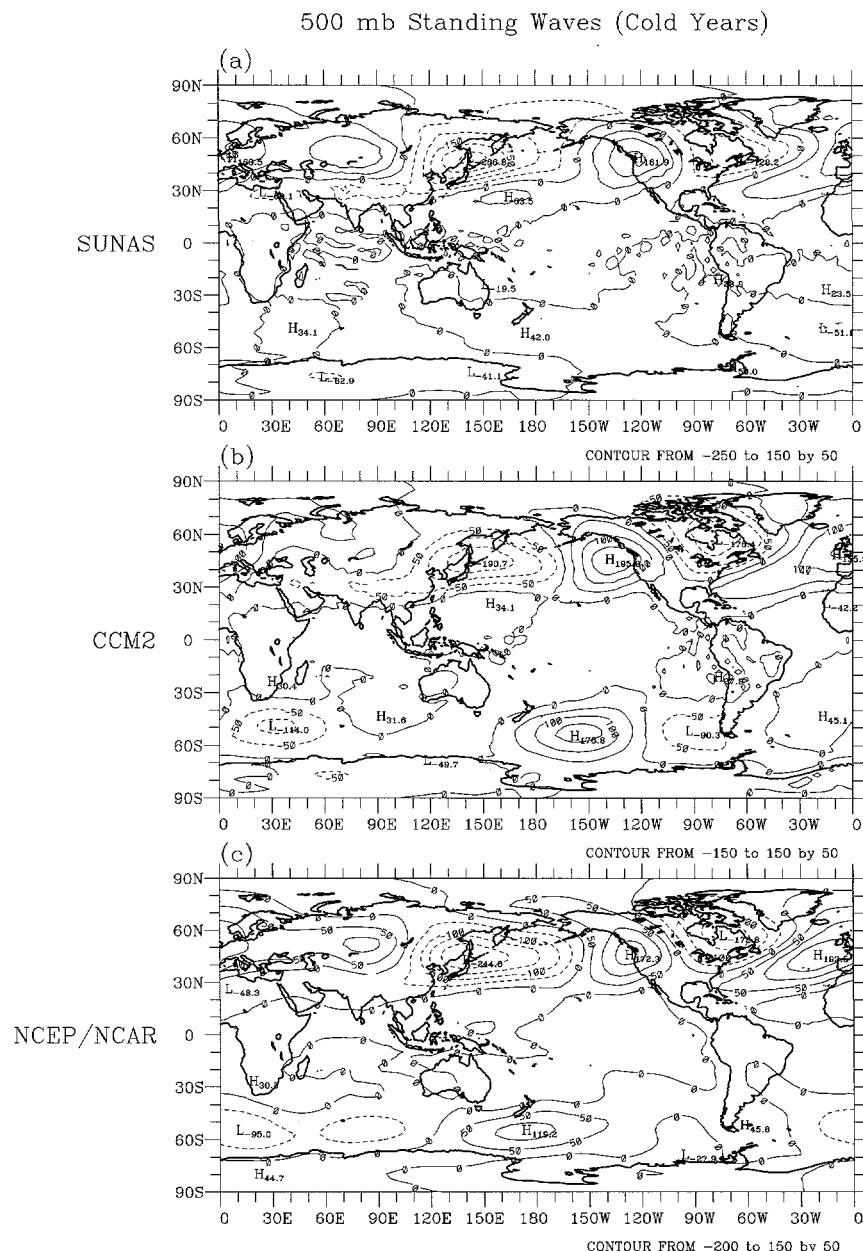
The objective of this project is to gain a fundamental understanding of the interactions between Earth's atmosphere and its oceans. We are focusing on improving models of processes in four main areas: numerical physics, cloud representation, water vapor observations, and the heterogeneous chemistry of aerosols. We have made advances in applying approximate inertial manifolds (AIMs), a method of dealing with subgrid-scale physics, to numerical computations of ocean models. We have developed a finite-difference version of AIMs for the shallow-water model equation, resulting in a large decrease in computing time with no loss in accuracy.

Our implementation of the now fully developed cloud parameterization package, SUNAS, into a global circulation climate model, CCM2, is showing remarkable improvement in simulating the hydrologic cycle (see first figure). Other parameters improved include the following: zonally averaged precipitation; overall cloudiness and precipitation patterns, particularly in the Amazon basin and the western Pacific; and persistent stratiform cloud decks observed in the eastern ocean basins.

We have used our shipboard lidar observations of water vapor in the equatorial Pacific to develop the first horizontal, two-dimensional maps of evaporative features in the ocean/atmosphere boundary layer. These maps show alternating patterns of dry and moist air indicative of rising and descending currents seen in laboratory convection experiments (see second figure).

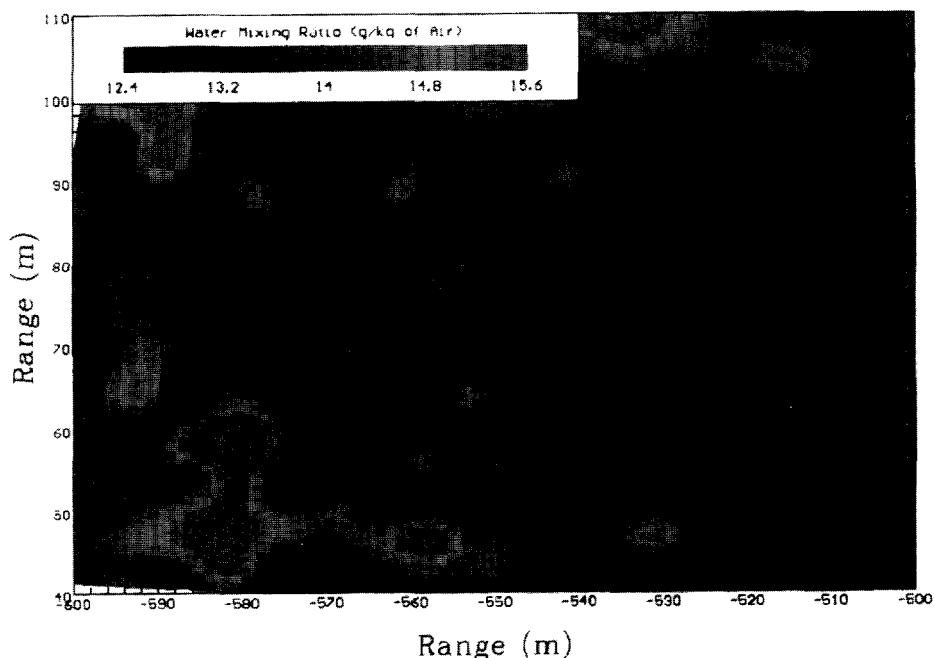
We have used advanced laser techniques to study heterogeneous processes on thin films that simulate stratospheric and tropospheric aerosol surfaces. In addition, we are quantifying adsorption processes mimicking

polar stratospheric cloud interactions with nitric acid trihydrate, a major component in ozone depletion.



These simulations show departure of 500 mb from the zonally averaged geopotential height (analogous to pressure) for cold years. These simulations were made using global circulation models (a) SUNAS and (b) CCM2 and are compared with data from (c) observations.

This plan view of water vapor concentrations 10 m above the equatorial Pacific Ocean shows patterns of dry and moist columns reminiscent of classic convection.



Publications

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- Zhao, X.-P., R.P. Turco, et al., "Numerical Simulation of the Dynamical Response of an Arctic Vortex to Aerosol Associated Chemical Perturbations in the Lower Stratosphere," *Geophys. Res. Lett.* **12**, 1525 (1996).

Transport Processes in Space Plasmas

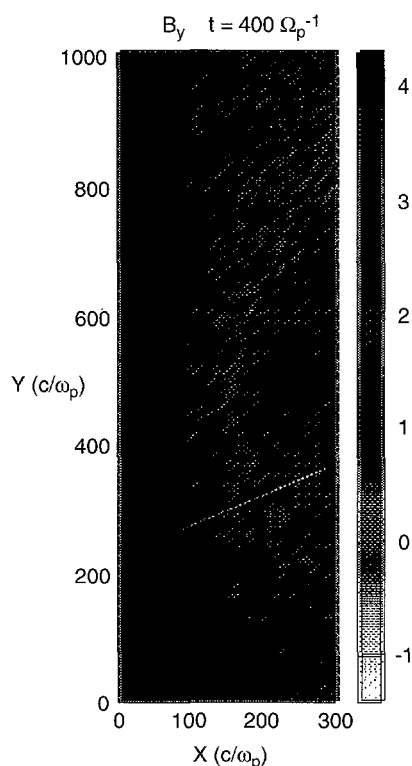
Joachim Birn

In this project we combined efforts in space-data analysis with theory and laboratory and computer simulations to advance the fundamental understanding of solar-terrestrial interaction through space-plasma processes.

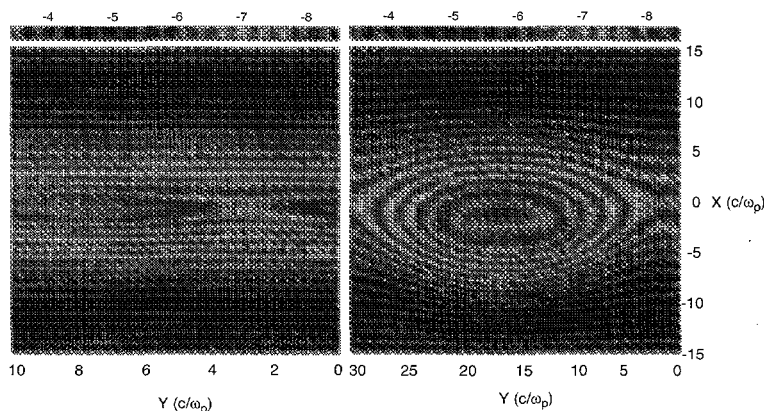
Two-dimensional simulations of the magnetopause have shed further light on the nature of surface waves and their contribution to ion diffusion in this boundary region. In these simulations a curved bow shock, its associated foreshock, and a turbulent magnetosheath are formed as shown in the first figure. These simulations combine proper accounting for the microphysics with the provision of a global perspective of the boundary region.

We have also performed the first high-resolution, full-particle (implicit) simulations of the guide field tearing at the magnetopause, using large ion-to-electron mass ratios. We found that, in sharp contrast to previous nonlinear theories, the multimode tearing islands can grow to large amplitudes, resulting in large transport of magnetic flux and mixing of the magnetosheath and magnetospheric plasmas as seen in the second figure. We developed a new nonlinear theory of the tearing mode at the magnetopause.

We have further studied the consequences of the electromagnetic proton anisotropy instability in the terrestrial magnetosphere. We used one-dimensional hybrid computer simulations to examine the velocity distribution response of both hot (~ 10 -keV) and warm (~ 10 -eV) protons. Results are that the enhanced fluctuations from this instability not only preserve the initially bi-Maxwellian character of a hot-proton distribution, but also drive an initially nongyrotropic hot distribution rapidly toward the gyrotropic condition.



Bow shock structure in a large-scale, two-dimensional simulation of solar wind-magnetosphere interaction. The figure shows the intensity of the magnetic field component B_y (as indicated by the color bar) in the coordinate frame x, y . The y -axis units (c/ω_p) represent the ion inertial scale length.



Magnetic island structure in simulations of tearing modes at the magnetopause. Left panel: single mode. Right panel: multimode with island coalescence.

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Physical Properties and Mantle Dynamics

Thomas Shankland

Understanding the physical properties of minerals and rocks reveals processes in the earth and events in its history. Because planetary interiors are difficult to assess, research methods that combine sophisticated techniques and associated theory are essential for interpreting geophysical field measurements in terms we need for improving our understanding of Earth's temperature, composition, stress state, history, and hazards. One objective of our project is to study minerals and rocks using materials science methods; another is to develop new research methods, such as high-pressure techniques, rock physics computational codes, and nuclear-based analyses.

In the past year, we continued to refine our transient optical-grating apparatus, which we have used to determine sound velocities in fluids and water ice at high pressures, and to fine-tune our single-crystal x-ray diffraction apparatus, which can be used to analyze materials at extremely high pressures and temperatures.

In addition, we have designed computational tools for forward and inverse modeling of complex stress-strain histories of rocks. Furthermore, by analyzing the ratio of tungsten to thorium in samples of bulk silicate rocks, we determined that tungsten depletion is of the same order as depletion of the iron and nickel that form Earth's metallic core. This result agrees with the hypothesis that Earth formed heterogeneously, that is, with dense materials accreting ahead of lighter ones. And finally, we have obtained pressure-volume-temperature equation-of-state measurements on single crystals and seismic velocity measurements on several dense minerals, which enables us to better understand the composition of Earth's outer 1000 km.

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Nuclear and Particle Physics

Advanced Research Capabilities for Neutron Science and Technology—Neutron Polarizers

Robert Robinson

The purpose of this work is to apply the expertise at both Los Alamos and at the National Institute of Standards and Technology (NIST) in polarized gaseous ^3He to research the development of new laser-driven ^3He polarizers suitable for condensed-matter research at the Manuel Lujan Jr. Neutron Scattering Center (MLNSC) at Los Alamos. Helium-3 polarizers are the technology of choice for broad-band applications at wavelengths below $2 \text{ \AA}$ and for large-divergence applications at all neutron wavelengths.

This project involves developing the experimental design, including the laser, glass cell, magnetic shielding and neutronics, then testing the cell both on the surface profile analysis reflectometer (SPEAR) and on a diffractometer. By the end of the project, we expect to know enough to implement this technology on any of

the spectrometers or diffractometers at MLNSC, although such implementation will not be covered by the project. If successful, our work would allow significant improvement in capability in neutron scattering to be implemented at Los Alamos.

So far, we have purchased all the instrumentation necessary to polarize a cell and measure its polarization. We now have three 16-W diode laser arrays and are collaborating with NIST, Princeton University, and the Tri-University-Meson Facility (British Columbia) for cell fabrication and filling. Together we chose a cell geometry suitable for condensed-matter applications and assembled all the components for the neutron-beam experiment. We requested beam time on the SPEAR at MLNSC in preparation for testing the polarizer early next year.

Solution Structure of the cAMP-Dependent Protein Kinase

Jill Trehwella

Understanding the molecular basis for biochemical regulation is a fundamental problem in human medicine. Unregulated or uncoordinated activities generally lead to pathological conditions and, if not corrected, to uncontrolled proliferation or cell death. In this project, we are addressing this fundamental question by studying the cAMP-dependent protein kinase, which has served as the central model for modulation of cell function by protein phosphorylation, one of the most important mechanisms of cell regulation.

Protein kinase is a dimer of dimers (R_2C_2), where C and R designate the catalytic and regulatory subunits, respectively. Free C is fully competent to catalyze the phosphorylation of proteins. The catalytically inactive holoenzyme is activated when cAMP binds to R, which exposes the catalytic site on C, allowing access to protein substrates.

The three-dimensional crystal structures of free C and R have been solved, providing a basis for modeling the holoenzyme using scattering data. We have succeeded in cloning and expressing both C and R and, in the case of R, have produced the expressed

protein in deuterated form. We have also demonstrated that we can reconstitute a catalytically competent holoenzyme from the expressed components, and we have measured x-ray scattering data from free C and R subunits as well as reconstituted holoenzyme with deuterated and nondeuterated R.

We are preparing for a neutron contrast-variation study on the holoenzyme with deuterated R. This experiment will yield the shapes and disposition of the R and C components in the complex, giving the first structural insights into the nature of the interactions between R and C.

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Development of Biosensors and Bioprobes Based on Spectroscopic Monitoring of Enzymes and Other Proteins Encapsulated in Sol-Gel Glasses

William Woodruff

This project sought to explore and develop new types of biosensors and bioprobes in biotechnology. Biosensors detect and measure analytes using the encapsulated biomolecules, while bioprobes examine the encapsulated biomolecules to elucidate their physiological/biochemical functions or structures. Our goal was to apply advanced spectroscopic methods to biosensors and bioprobes whose sensing elements consist of enzymes and other proteins encapsulated in optically transparent sol-gel glasses.

Our specific objectives were (1) to characterize encapsulated biomolecules and their interactions with a porous glass matrix and monitor the effect of different processing conditions using spectroscopy and kinetics, (2) to similarly characterize interactions of the encapsulated biomolecules with potential substrates or ligands, and (3) to apply the above information in developing sensing elements for use in biosensors and bioprobes. Major results included the characterization of encapsulated myoglobin and its

reactions with ligands in the glasses and the spectroscopy and kinetics of relevant myoglobin reactions in solution.

Techniques were developed for observing the kinetics of reactions at elevated pressures of gaseous ligands.

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Molecular Characterization of Flow-Sorted Mammalian Centromeres

*L. Scott Cram, Los Alamos National Laboratory
Barbara Hamkalo, University of California, Irvine*

To better understand the fundamental mechanisms underlying such cellular processes as the regulation of gene expression, differential condensation, and chromosome segregation, we are interested in isolating and identifying the proteins from the centromere region of mammalian chromosomes.

The goal of our project is to employ flow cytometry to isolate large quantities of both intact mouse chromosomes and a chromosome fragment derived from centromere regions to biochemically compare the protein composition of the two fractions. This is a novel approach to identify proteins preferentially associated with centromeres that could play a role in centromere higher-order structure and/or function.

Initial chromosome sorts, utilizing buffers developed by Los Alamos researchers for genomic cloning, resulted in samples devoid of detectable amounts of protein, although they contained measurable amounts of DNA. Based on a series of control experiments, we determined that chromosomal proteins were being displaced from the DNA into the supernatant before sorting. An extensive analysis of each component in the sorting buffers showed that three components—EDTA, EGTA, and mercaptoethanol—were responsible for extracting all but a few chromosomal scaffold proteins. This displacement occurred despite the fact that by fluorescence microscopy, the chromosomes appeared to retain their structure.

We hypothesize that spermine and spermidine (two components of the buffers) exchanged for proteins, resulting in compact chromosomal structures.

Utilizing a 10-mM MgSO_4 , 10-mM KCl, 5-mM HEPES buffer (pH 8), the flow cytometer can sort chromosomes without any apparent loss of proteins. Inclusion of the reducing agent dithiothreitol in the sorting buffer improves the resolution of chromosomes during sorting without protein loss. We can reproducibly observe a large number of polypeptides, in addition to the histones, by SDS-PAGE (sodium dodecyl sulfate-polyacrylamide gel electrophoresis) and by silver staining gels containing proteins released from approximately 200,000 chromosomes per lane.

With the results of this study complete, we will now characterize these proteins and extend our methods to recovering and characterizing proteins from other chromosome types and regions.

Advanced Biomolecular Materials Based on Membrane-Protein/Polymer Complexation

Gregory Smith

The goal of this work has been to (1) develop a fundamentally new class of bioactive molecular films composed of reconstituted and native, self-assembled, membrane proteins combined with polymers and (2) apply synchrotron-based, small- and wide-angle x-ray scattering to characterize the structure and phase behavior, the interlayer and macromolecular forces, and the stability of the protein-shape of these new materials. These materials can be used as biosensors, selective filters, and light-to-chemical energy converters.

We have completed the first series of high-resolution, synchrotron, x-ray scattering studies of the purple membrane composed of a two-dimensional

(2-D) self-assembly of the membrane protein bacteriorhodopsin. At high humidity, the ordered phase of this highly complex self-assembly exhibits scattering characteristics of a 2-D solid with power-law decay of positional correlations. Two results of the x-ray scattering measurements are (1) the first measurements of a protein-lattice elastic rigidity, which is directly related to the protein-protein interactions, and (2) an experimental demonstration of the limits on the resolution of the protein structure in 2-D protein crystallography (an expanding field because of the recent success of techniques for preparing 2-D protein crystals).

To enhance the structural work, we initiated a series of neutron

experiments. First we constructed a simple humidity oven with neutron-transparent windows for reflectivity studies. We prepared thin-film samples by spinning protein mixtures onto silicon wafers. To hydrate the films, we placed each in this sealed oven with a reservoir of D_2O (heavy water) and measured the room-temperature, neutron reflectivity at the High-Flux Beam Reactor at Brookhaven National Laboratory. In each case, the reflectivity measurement was consistent with a bare silicon surface. Upon optical examination of the samples, we found that the multibilayers had delaminated from the silicon substrate, leaving droplets of sample on the surface.

While the spinning technique shows promise in preparing the films necessary for the reflectometry experiments, these results suggest that the films must be deposited on etched silicon, very clean quartz, or surfaces that have been altered with silane to produce a high degree of hydrophobicity.

Similarity Landscapes: An Improved Method for Scientific Visualization of Information from Protein and DNA Database Searches

Norman Doggett

The focus of this project is to study the evolution of human and simian immunodeficiency viruses (HIV). As the viral genomes diverge, it is possible to monitor the ratio of meaningful to silent changes at the RNA level and determine the intensity of the selection that is operating on them.

This year we have developed a method for distinguishing transitional and transversional changes of these two types and find that both types of change often show a pattern of intense directional selection that has driven the

separation of closely related viruses, particularly HIV-1. This directional evolutionary change is concentrated in short tripeptide motifs called sequons. These sequons are sites of n-glycosylation, and the proteins of retroviruses have unusually large numbers of sequons. We have found that sequons have evolved more rapidly in the more virulent HIV-1 than in the less virulent HIV-2, and calculation of the relative rates indicates that they have evolved three times as rapidly compared with the rate of substitutions

at the RNA level. We have used our capabilities for rapid searches of the entire database in GenBank to examine the properties of microsatellites, regions of DNA that consist of multiple repeats of a short (usually 2- to 6-base) sequence, in lower organisms. We have discovered that microsatellites are far more prevalent in lower organisms, even prokaryotes, than had previously been realized, that many of these microsatellites occur in reading frames, and that a large fraction of them are polymorphic. Ten out of ten of the in-frame microsatellites examined in the yeast *Saccharomyces cerevisiae* were polymorphic.

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Formation of Drug-Bearing Vesicles in Mixed Colloids of Bile Salts and Phosphatidylcholine

Rex Hjelm

We are examining novel methods of forming drug-bearing liposomes. Liposomes have proven to be effective as intravenous delivery systems for insoluble drugs. We are studying systems that could potentially form liposomes spontaneously, such as biological mixed colloids, as a better alternative to the presently used mechanical means of liposome production. Because liposomes are formed spontaneously in these systems, the formulations could be stored in dry form and reconstituted by the addition of appropriate buffers, thus reducing the need for costly equipment and procedures and improving shelf life considerably. We need to show the conditions and drugs that do not interfere with the spontaneous formation of liposomes. The study of these colloids also relates to the efficacy of oral formulations, because drug-bile

interactions could be responsible for the bioavailability of oral drug formulations. Therefore, we are also studying the particle structure in simulations of the intestinal mixture to test whether the bile salt/phosphatidylcholine systems are good models of drug-bile interactions in the intestine. We are studying these systems using small-angle neutron scattering, supplemented by light scattering.

We have shown that the inclusion of therapeutic levels of the steroidal drugs, cholesterol, progesterone, hydrocortisone, and deoxycorticosterone, does not affect liposome morphology. These results support our theory that mixed colloids have a valuable role in drug delivery. Further, we have shown that particle morphology in bile salt/phosphatidylcholine particles is the same as that found in the intestine, allowing us to test models of bile-drug

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Structural Biology of Disease-Associated DNA Repeats and Protein-DNA Complexes Involved in the Repair of DNA Damage

Goutam Gupta

This work focused on examining the structural biology of the DNA triplet repeats associated with genetically inherited neurological disorders such as fragile X, Myotonic Dystrophy, and Huntington's disease. (The accompanying schematic demonstrates how the number of such repeats is related to the expression of fragile X syndrome.)

We have used two-dimensional nuclear magnetic resonance spectroscopy, nondenaturing gel electrophoresis, and digestion by single-strand-specific P1 or S1 nuclease to demonstrate that the triplet repeats found in the genes causing these neurological disorders adopt hairpin structures (i.e., a single strand of DNA loops back to base-pair with itself rather than with its

complementary strand) under physiological solution conditions. We have also demonstrated that the same hairpin structures are formed during replication, leading to slippage, which in turn contributes to the observed length polymorphism.

Furthermore, we have carried out biochemical assays with human methyltransferase that demonstrate that the same hairpin structure that causes slippage and length polymorphism is also an excellent substrate for methylation, and we found that the fragile X triplet repeats are more sensitive to methylation than many other DNA regions, especially when they have been expanded. The accompanying sketch shows a possible mechanism of expansion and methylation.

Publications

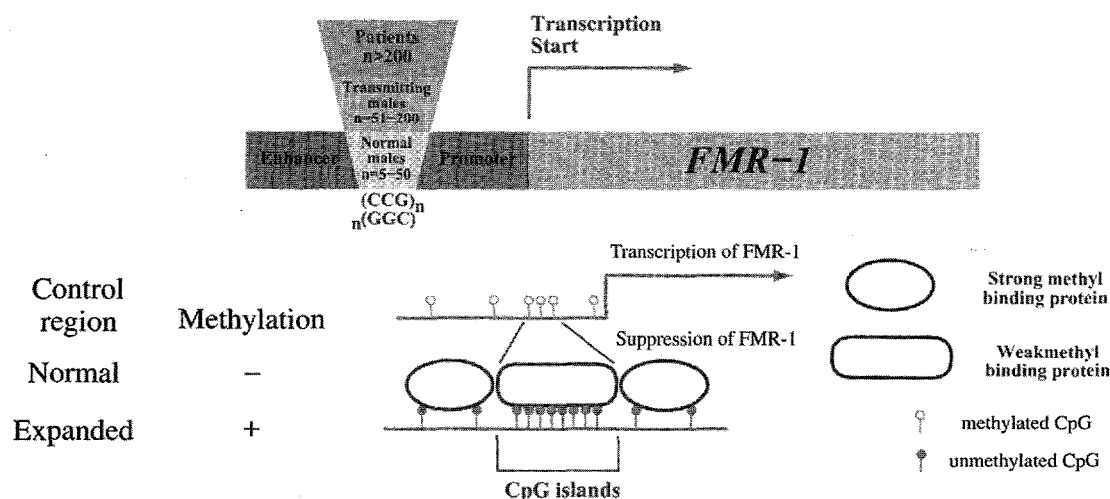
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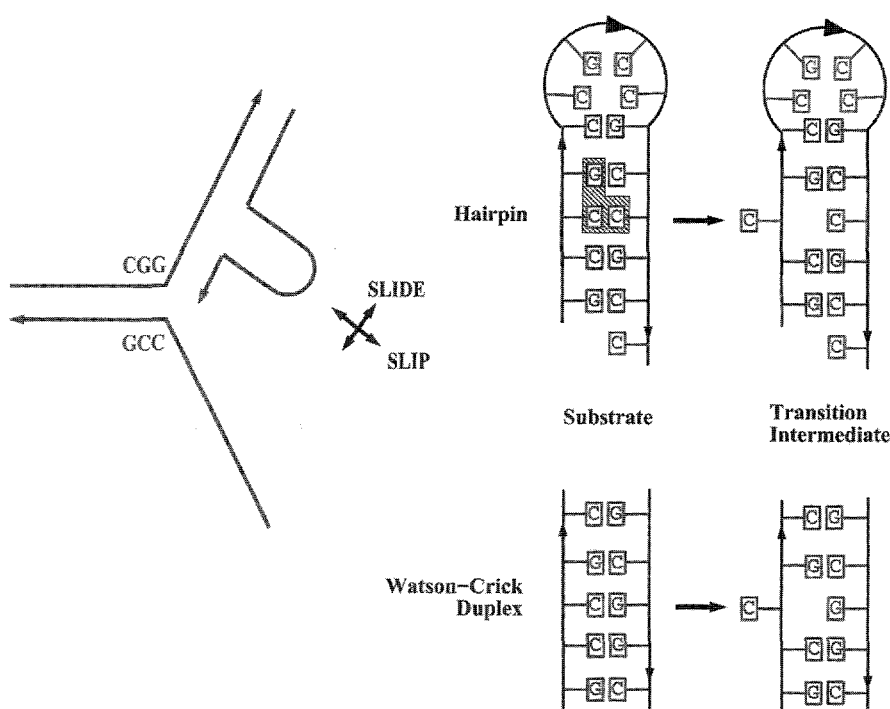
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A schematic representation of the *FMR-1* gene. The location of the fragile X repeat, $(GCC)_n \cdot (GGC)_n$ is shown in the 5' untranslated region, although the exact location and the interrelationship of the promoter and the enhancer are not yet known. The ranges of repeat numbers, n , are shown for normal, transmitting, and affected males.

A sketch of how the presence of a transient and mobile three-way junction can cause both expansion and methylation. The intrinsic preference of hairpin formation by the GCC strand leads to a three-way junction with a Watson-Crick anchor. When the GGC strand acts as the template, such a three-way junction leads to expansion if the GCC hairpin escapes repair. In the GCC hairpin of the three-way junction, the Cs are C•C paired, rather than C•G paired as in the Watson-Crick duplex. One of the Cs from a C•C pair is more susceptible to being "flipped out" of the duplex and methylated than a C from a C•G pair. The GCC hairpin at a three-way junction is also capable of slipping and sliding, which can make the C•G pair in a hairpin "slip" one notch to create a C•C pair.



Applications of Optical Trapping to Single-Molecule DNA Sequencing

Richard Keller

We are investigating whether we can use optical laser trapping (i.e., optical tweezers) for single-molecule DNA sequencing and single-molecule detection (SMD). Single-molecule DNA sequencing involves selecting the fragment to be sequenced, synthesizing the complementary strand using fluorescently labeled nucleotides, attaching DNA fragments to host substrates (microspheres) anchored in a flow stream, sequentially cleaving the end nucleotide with an exonuclease to release the labeled nucleotide into the flow stream, and using laser-induced fluorescence to detect and identify the dye-tagged nucleotides. We are currently using a pipette to hold the microsphere containing DNA in the flow stream. This project involves investigating the applicability of optical laser trapping as an alternative method of holding the microsphere in the flow stream. We can use the radiation trapping

forces associated with a highly focused laser beam for this task.

We successfully demonstrated optical trapping in laminar flow streams and completely characterized the trapping process as a function of fluid flow velocity, chamber dimension, trapping depth, incident laser power, and fluorescence measurement geometry. In particular, we integrated an optical laser trap with fluorescence excitation/emission capability in a flow cytometric geometry so that we could study microparticle confinement and off-axis fluorescence detection. At the trapping wavelength of 1064 nm, we simultaneously trapped and displaced 2- μ m-diam fluorescent latex microspheres by up to ± 20 μ m; we did this by scanning the trapping beam in directions parallel and perpendicular to the flow stream, while we measured particle fluorescence. With fluorescence signal-to-noise ratios in excess of

30 dB, we trapped and measured particles in flow streams that had velocities of up to 12 mm/s. We showed that samples can be noninvasively positioned either upstream or downstream from the detection probe volume, a feature integral to SMD implementation. In a stationary fluid, we demonstrated trapping of 2.8- μ m paramagnetic beads that were coated with lambda DNA. However, because of significant variations in the optical and magnetic properties of these substrates, we could not trap DNA-coated beads consistently and reliably in the present system.

Publications

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Microbial Acquisition of Iron from Iron-Bearing Minerals

Larry Hersman

Iron is a universal nutrient requirement for all life forms. Although the fourth most-abundant element in the geosphere, iron is virtually insoluble under environmental conditions (neutral pH, oxic), where it exists mainly as very insoluble oxides, hydroxides, and oxyhydroxides. We do not completely understand how iron is solubilized and made available for biological use. The overall objective of this research was to determine, in part, some of the mechanisms used by microorganisms to acquire iron from hematite.

In the past we have reported on the dissolution of hematite by microbially produced, iron-binding ligands called siderophores. During this past year we investigated the role of other metabolic products on the dissolution of hematite. Of particular interest were high-performance liquid chromatography (HPLC) compounds that eluted from a C-4 column before the siderophores. These pre-siderophore

compounds, or peaks, were of interest because with increased incubation time (of the microorganisms in the presence of hematite), these peaks became larger. In other words, exposure to hematite appeared to induce the production of these metabolic products.

We performed a series of assays to determine the role of HPLC compounds in hematite dissolution. Specifically we investigated the potential of these HPLC compounds to reduce iron or to serve as electron-transport molecules (i.e., ligand bridges) between a reductant and iron. Results of these reduction assays suggest that these compounds are capable of serving as ligand bridges between a reductant nicotinamide adenine dinucleotide (NADH) and iron. Although strictly an aerobic species, this particular species of *Pseudomonas* appears to use a special form of reductive dissolution to

acquire iron from hematite. To our knowledge, such a process is unique and previously unreported in the literature.

Publications

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The Biology of Novel Animal Genes: Mouse APEX Gene Knockout

Mark Macinnes

Apurinic/apyrimidinic (AP) endonuclease (APE), sometimes known as APEX, is involved in a key step in the repair of spontaneous and induced AP sites in DNA, in which an information-containing base is lost or damaged, essentially breaking the rungs of a cell's DNA ladder. APE removes the damaged part of the ladder so that another repair enzyme can rebuild it correctly. Efficient

repair of AP sites is essential for preventing such mutations from becoming stably incorporated into the cellular genome, which can cause the cell to die or become cancerous. Loss or modulation of repair enzymes such as APE may elevate the spontaneous mutation rate in cells and may lead to a substantial increase in the incidence of cancer.

Despite extensive biochemical analysis, the biological significance of the multiple enzymatic functions of APE in vivo has not been determined. The goals of this project are to conduct preliminary genetic, biological, and cellular characterizations of mice containing a nonfunctional version of the APE gene—mice whose APE genes have effectively been "knocked out."

Using gene targeting strategies, we have generated mouse embryonic stem (ES) cells that are heterozygous for a deletion mutation in the APE gene (that is, they contain one normal

and one nonfunctional APE gene). We have subsequently produced whole animals, derived directly from the heterozygous ES cells, containing this APE mutation. These animals are overtly normal and do not display any adverse effects of the mutant APE allele. However, by inbreeding these mice, we have determined that animals which are genetically homozygous for the APE null mutation (designated APE^{-/-}) die early in gestation.

We have shown, through genetic and histological analyses of early stage embryos (days 3.5 to 11.5 of a 20-day mouse gestation period), that loss of the APE gene product does not affect blastocyst formation or implantation. However, at or around day 7.5, during a period of substantial cellular differentiation and expansion, APE^{-/-} embryos begin to fail in normal development. These embryos display a variety of abnormalities and do not progress further than day 7.5 of

development, although embryo remnants have been identified at day 9.5 of gestation. APE^{-/-} embryos were not found later than this period, and preliminary evidence suggests that the developmental failure in these animals induces apoptosis, or programmed cell death (essentially cell suicide), which results in complete embryonic death between 7.5 and 9.5 days of gestation. These results underscore the essential functional significance of this DNA repair gene during normal embryonic development.

Competency Development in Antibody Production for Cancer Cell Biology

Min S. Park

Investigating the roles that proteins play in complex biological processes requires the use of antibodies against specific cellular proteins. The objective of this project is to develop the technical capabilities, including the use of recombinant technology, for producing high-quality antibodies that can be available for research on cancer development.

Our work includes both conventional and recombinant antibody-producing technology. The conventional method involves purifying cellular proteins, or antigens, and injecting them into an animal, which in turn produces antibodies to the antigen. Recombinant techniques involve isolating the genes that code for the desired antigen or antibody and inserting the genes into an expression vector. Recombinant technology enables us to make large quantities of high-quality antibodies. Controlled expression of an antibody gene that is specific to tumor antigen provides another novel approach for immunocancer therapy.

In the past year we continued to produce antigens and antibodies critical to identifying and monitoring the expression of crucial proteins involved in cell-cycle checkpoints, the regulation of cell division, and the rate-limiting steps of DNA repair. Specifically, we produced three more antigens (total now is eight over the entire project period), two more antibodies (total now is five over the entire project period), using conventional approaches. We also produced a library of antibody genes that encode recombinant antibodies.

Publications

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Covariation of Mutations: A Computational Approach for Determination of Function and Structure from Sequence

Alan Lapedes, Los Alamos National Laboratory
Melissa Cline, University of California, Santa Cruz
David Haussler, University of California, Santa Cruz

One of the foremost problems in molecular biology is understanding protein folding—what processes transform proteins from simple linear sequences to elaborate structures of helices, sheets, and turns. Many researchers use Newtonian-mechanics-based molecular dynamics to convert amino acid sequences into three-dimensional forms, but this approach is cumbersome and is not as accurate as desired. In this project, we take a different approach in our study of inverse protein folding. Inverse folding approaches attempt to match an amino acid sequence to a library of known structures. "Inverse," therefore, refers to the process of working "backward," using many known structures to determine the folding endpoints of a new sequence. (In contrast, most conventional approaches start with amino acid sequences and little, if any, reference to known structures.) We expect our work on inverse protein folding to bring to light enough new knowledge on the relationship between structure and sequence to facilitate great progress on better understanding protein folding in general.

In the past year, we expanded the linear Hidden Markov Model software, a probabilistic pattern recognition program originally designed for speech recognition, into a functioning protein structure predictor. To test the software, we built a model library that contains models for approximately 1000 protein families, and we used this library to predict the structure of most of the proteins in one family. In

two cases, as part of the CASP-2 structure prediction contest, we predicted the folding of a sequence before its structure was determined, and in both cases, our predictions were experimentally verified.

We have also enhanced our tool suite to include a graphical, RASMOL-based alignment viewer and scoring options so we can accommodate different model lengths. Upcoming features include a weighting scheme that builds on phylogenetic relationships and emphasizes the alignment columns most critical to the structure or function of a protein.

We have also continued to develop a neural net method for modeling beta sheet interactions. Based on a protein's amino acid sequence, as well as other physical properties including chain separation and beta strand membership, we can estimate the likelihood that two beta strands will be in contact. We plan to incorporate this beta sheet modeling capability

into our structure prediction software during the next year.

Finally, we have continued our work on neural-net-based scoring functions to quantify the matches between sequence and structure in inverse folding investigations by increasing the spatial resolution and accuracy of our models.

Publications

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Structure, Dynamics, and Function of Biomolecules

Hans Frauenfelder

Our project is aimed at enhancing Los Alamos' core competency in experimental techniques, theory, high-performance computing, and modeling. Our main focus is on simulating and understanding biomolecular structure, dynamics, and function. In particular, we are developing scattering techniques to study the structures of biomolecular complexes in solution.

One of our primary goals has been to increase—by a factor of 10—the intensity of the existing low-Q neutron diffractometer (LQD) at the Manuel Lujan Jr. Neutron Scattering Center at Los Alamos. This increase would result in a dramatic improvement in its application to structural biology studies.

We used Monte Carlo modeling methods to design and test a number of upgrades to the LQD that would increase the flux of neutrons on our biological samples (see accompanying figure). Specifically, we designed the following:

- a five-hole multiaperture collimator, which allows a sample to “see” a larger area of the neutron source (moderator) and, hence, to capture more total neutrons;

- the T_0 chopper, which minimizes unwanted background; and
- the variable detector position, which allows for better optimization of resolution and neutron flux for individual experiments.

We will implement and test these upgrades in the next project year.

We have also designed an LQD for a next-generation long-pulse spallation source. In the area of structural biology applications, we have used neutron scattering to complete work on a receptor/ligand complex as well as a protein/DNA complex important in DNA damage repair.

To strengthen interactions between theory and experiment and between the biological and physical sciences, we have communicated our work and goals at regular meetings of researchers from all interested Laboratory organizations. In addition, we are conducting a distinguished lecture series on Issues in Modern Biology and are using the forum to discuss the directions of the field and, in particular, our work. In total, 17 distinguished lecturers (7 of whom were

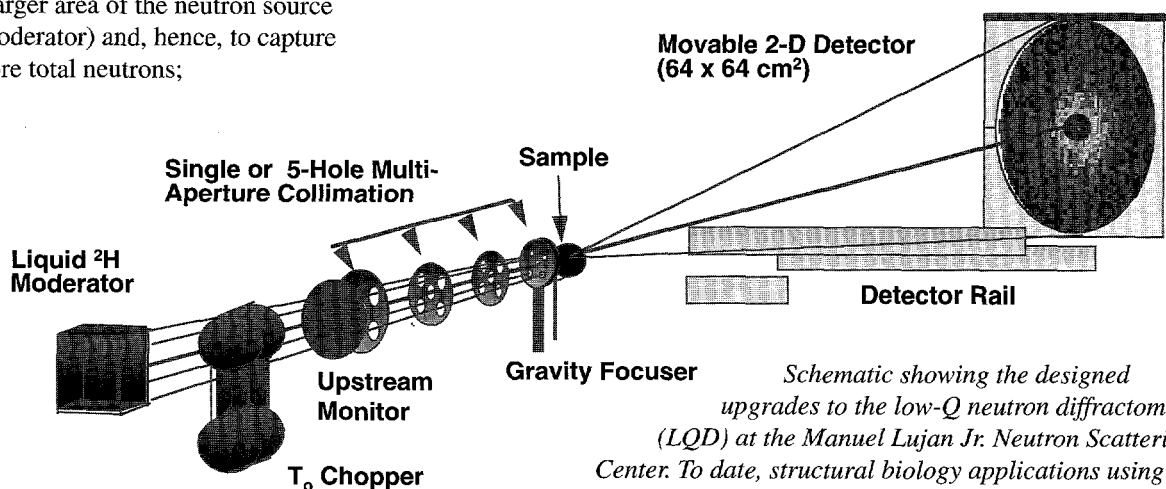
Nobel Prize winners) have given presentations at this series of discussions.

Publications

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Schematic showing the designed upgrades to the low-Q neutron diffractometer (LQD) at the Manuel Lujan Jr. Neutron Scattering Center. To date, structural biology applications using LQD have been limited by the neutron flux on this instrument. The designed improvements will result in a dramatic increase in its application to structural biology studies.

Advanced NMR Technology for Bioscience and Biotechnology

Jill Trehwella

Nuclear magnetic resonance (NMR) technologies play critical roles in bioscience and biotechnology in both imaging and structure determination. The major issues limiting the application of NMR to many important problems are the inherent low sensitivity of the NMR experiment and the spectral resolution required to study biological molecules. This project addresses both of these issues by working on the development of (1) magnetic resonance force microscopy with the long-term goal of imaging individual biological molecules and (2) high-magnetic-field NMR with isotope labeling to overcome current limitations on the size of biomolecules whose structures can be determined using multidimensional NMR.

In the past year we have developed a novel radio-frequency coil design for NMR force microscopy applications that are pushing the limits of sensitivity in magnetic resonance detection for imaging, and we have demonstrated subsurface spatial

imaging capabilities. We have also made advances in the miniaturization of two critical magnetic resonance force microscope components: the micromechanical resonator and the micromagnetic tip. In the area of high-field NMR and isotope labeling, studies have been completed on the muscle protein troponin C complexed with segments of its regulatory target troponin I. This complex is responsible for the regulation of muscle contraction and is too large for study using conventional NMR approaches. As is the case for the vast majority of biomolecular complexes, the complex has limited solubility, resulting in even more demands on the NMR experiment. Using state-of-the-art, high-field NMR instrumentation at Pacific Northwest National Laboratory, we have measured NMR data from complexes of isotopically labeled troponin C complexed with key sequence segments of troponin I. We have successfully interpreted these data in terms of structural information on the troponin I component.

Publications

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Hernandez, G., S.E. Rokop, P.A. Springer, et al., "NMR Studies of Troponin I(96-115): Free in Solution and Bound to Troponin C," *Biophysics J.* **70**, 384 (1996).

Hoyt, D.W., J. Zhao, et al., "Comparison of Small-Angle X-ray Scattering and Gradient Encoded NMR Diffusion Experiments for Assaying the Aggregation State of Proteins in Solution" (submitted to *J. Magn. Reson.*).

Trehwella, J., G. Hernandez, S.E. Rokop, et al., "High-Field NMR & Stable Isotopes for Studying Ca^{2+} -Binding Proteins and Their Complexes," *27th Annual Southeast. Magn. Reson. Conf. Proc.* **1**, 4 (1995).

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Nonlinear Analysis of Biological Sequences

David Torney

The purpose of this project is to develop effective new computational and mathematical techniques and apply them to analysis of the structure of biological sequences. We are currently focusing on the detection and characterization of functional domains. We are also modeling multigenic human diseases with the goal of designing more effective experiments that will discover the genetic components of these diseases.

We have established the usefulness of parities of subsequences for classifying binary sequences. To use this approach for DNA sequences, we first converted these subsequences to binary sequences. We determined the average parities for subsequences of 54-base-long coding sequences, for which the frame and strand were known, and for noncoding sequences. We found that the subsequences with the smallest number of letters were

most discriminatory, and use of these subsequences yielded a correct classification rate of 0.82 for both types of sequences—the best success rate yet reported for such short sequences. We have begun to develop sophisticated statistical methods for combining the parities from many subsequences, since we employed several thousand, as a classification technique. We explored cumulants, which yield an expected parity for a subsequence based upon its subsequences, and thus enable the winnowing of "key" subsequences. These simplest cumulants revealed novel

statistical features of coding and noncoding sequences.

Our characterization of protein-sequence motifs, conserved through evolution, was made much more effective by employing maximum likelihood techniques. By averaging over possible evolutionary histories, we derived accurate profiles for amino acid usage. Furthermore, this approach allows the quantification of coevolution of pairs of amino acid residues. Based on preliminary models, we found many more statistically significant pairs of coevolving residues than are yielded by other approaches and have corroborated these interactions through studies of molecules with known structure.

Publications

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Indigenous Bacteria as Hosts for Proteins for Bioremediation

James Brainard

Successful application of engineered proteins for in situ bioremediation requires efficient mechanisms to introduce and distribute the enhanced biological activity at the contaminated site. An attractive strategy to accomplish this process is through the use of bacteria native to the site as hosts for the engineered proteins. The goal of this project is to gain sufficient understanding of the coupled biological, chemical, and physical processes occurring at contaminated sites in order to rationally design and test this strategy. Although the project is primarily focused on a specific enzyme (Haloalkane dehalogenase) and specific *Pseudomonas* isolates, the results will have broad applicability to

many contaminants, unmodified and engineered proteins and genes, and microbial isolates.

During the first year of this project, we have made excellent progress in several areas: (1) isolating microorganisms into which to place genes for engineered Haloalkane dehalogenases, (2) developing the tools required to detect, track and measure genes in the environment, (3) developing methods to introduce and express broad-host-range plasmids containing engineered genes, and (4) using numerical simulations to identify which parameters are most important in limiting bioremediation effectiveness.

We have selected three sites that are contaminated with 1,2-dichloroethane

(DCA) from which to isolate indigenous hosts for engineered and wild type alkane dehalogenase genes. From one of these sites, we have begun enrichment cultures and direct plating to isolate Type I fluorescent *Pseudomonas* and other indigenous species capable of degrading DCA and intermediates of DCA degradation.

Publications

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Landscapes and Dynamics of Proteins

Hans Frauenfelder

The goal of the project is to understand the energy and affinity landscapes in physics and biology. Complex systems, such as biopolymers, glasses, and large martensitic crystals, have a highly degenerate ground state and can assume a large number of different structures. These characteristics are typically described by a rugged energy landscape. The dynamics within such a landscape are far more intricate than dynamics in simple systems, displaying hysteresis and sometimes showing the multi-scale character of an avalanche or a quake. Our goal implies some new directions in the study of nonlinear systems and closer interactions with theorists, computer experts, and experimentalists at Los Alamos National Laboratory and in a number of universities.

The project objective for the first year, which we met, was to learn more about the field from visitors, seminars, and workshops. Many visitors were invited to give talks both at the Center for Nonlinear Studies (CNLS) and also in the colloquium series "Issues in Modern Biology." The 16th CNLS Annual Conference was called "Landscapes." The conference included reports on experimental, theoretical, and modeling studies in glasses, spin glasses, biopolymers, hierarchical materials, neural networks, and evolution, and it attracted the best researchers in this field. The conference was reported in *Nature*.

In addition to the more formal discussions with visitors and at the conference and workshops, many discussions on theoretical and experimental aspects were held at CNLS. Partially as a result of these interactions, we proposed a new core-competency development thrust area for the Laboratory on structural biology, which involves collaboration among four divisions and is now active as an integrated structural biology resource.

Publications

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Engineering Haloalkane Dehalogenase for Bioremediation

James Brainard

Although bioremediation is potentially one of the most cost-effective environmental cleanup tools, present bioremediation practices have difficulty achieving effective destruction of some contaminants, notably halogenated hydrocarbons. Many microorganisms contain halocarbon degrading enzymes, but these enzymes are poor catalysts relative to other enzymes. Enzymes that work on xenobiotic halogenated contaminants suffer from poor affinity for the contaminant and slow turnover rates even when the contaminant is bound, and sometimes generate toxic intermediates. The goal of this project is to develop the tools and understanding required to engineer enzymes with enhanced properties for bioremediation of contaminants. To do this we design, construct, express, and test enzymes based on naturally occurring enzymes that degrade halocarbons.

These modified proteins have enhanced capabilities for degrading specific halogenated alkanes and may be optimized for in situ bioremediation strategies and waste stream treatment. Although our efforts are focused on engineering halocarbon-degrading enzymes, the results have application to other contaminants, in particular, other recalcitrant organics and both toxic and radioactive metals.

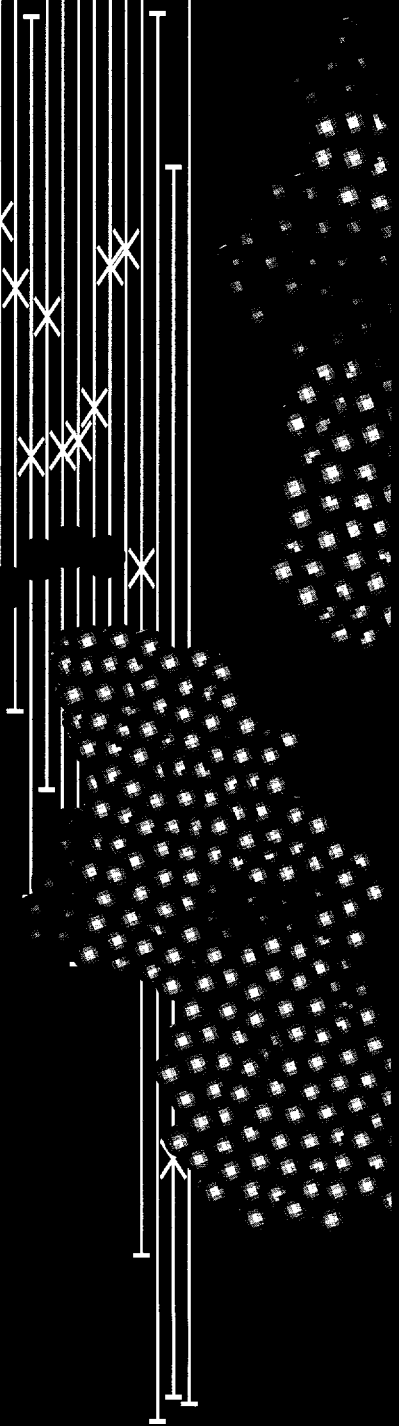
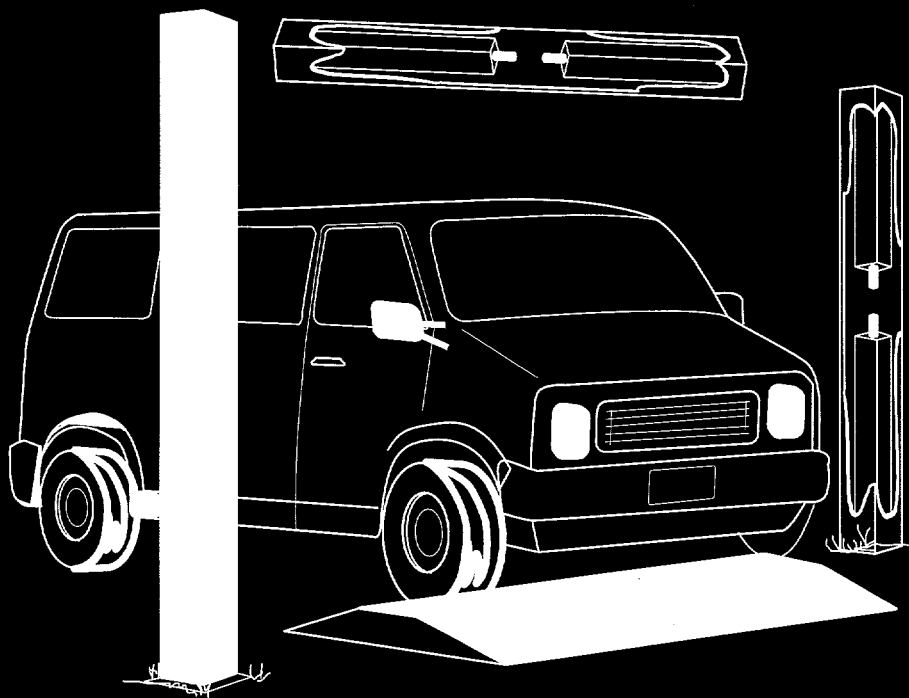
This year we have made excellent progress in (1) developing the molecular biology tools to allow rational and directed-evolution approaches to enzyme engineering; (2) developing the microbiological, analytical, and spectroscopic tools to screen, select, and characterize improved enzymes; (3) theoretical modeling of the chemical reactions, solvent interactions, and protein

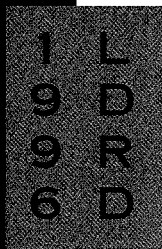
dynamics of dehalogenating enzymes; (4) developing and validating experimental models for understanding the effects of heme environment on enzyme dehalogenation functions; and (5) using cryocrystallography to trap reaction intermediates of cytochrome P450 and characterize their structure.

Publications

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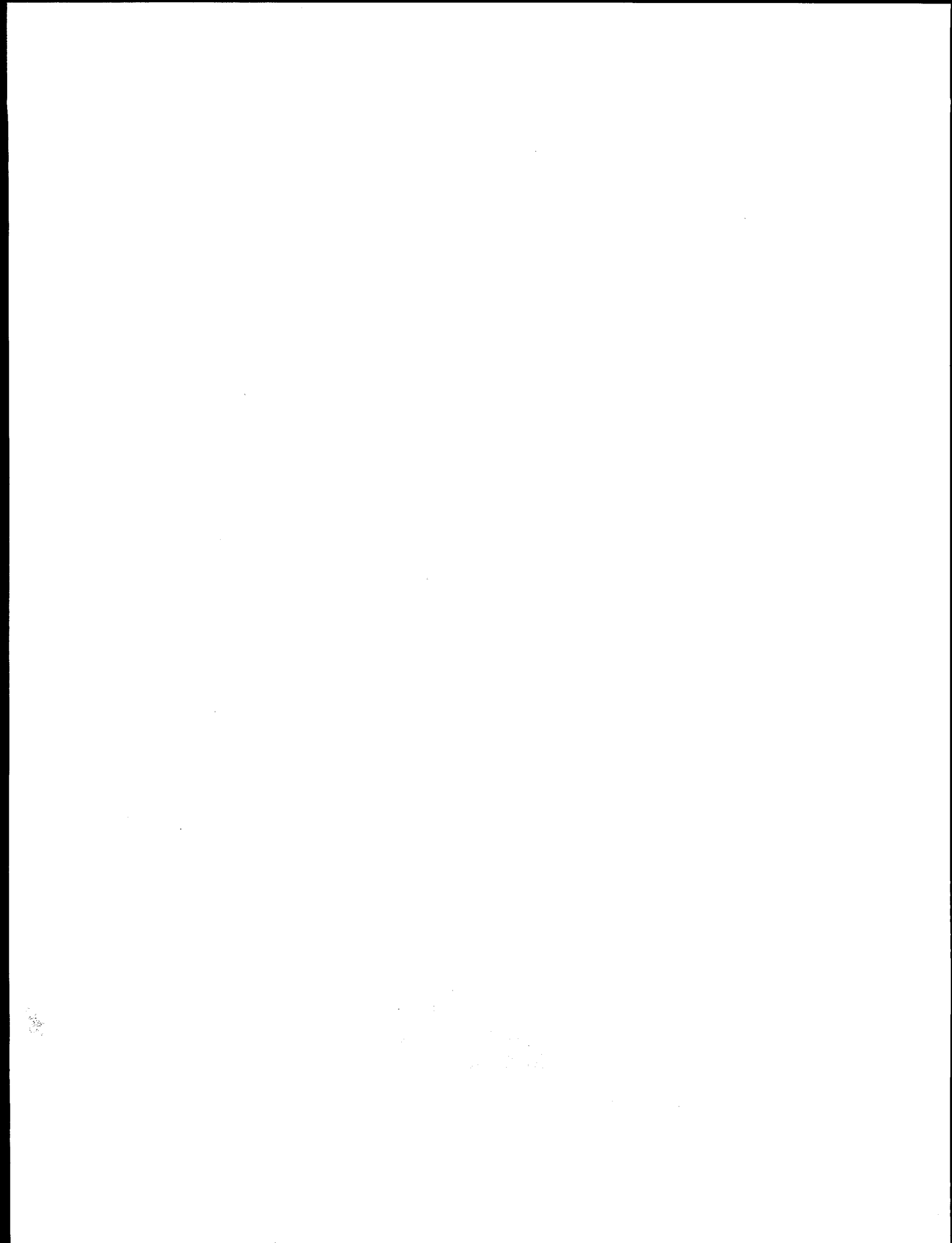




Program Development Projects

Program Development (PD) projects support R&D aligned with future programmatic opportunities at the Laboratory as guided by the Laboratory's strategic planning process. PD projects are selected by the Laboratory program directors to explore and develop technologies needed for emerging mission objectives in nuclear weapons, nuclear materials and stockpile management, nonproliferation and international security, conventional defense, environmental management, industrial partnerships, and energy. This year, PD projects accounted for 24% of the LDRD budget and 21% of all projects, and they supported research in all nine technical disciplines.

Examples of subjects investigated by PD projects include the effects of aging on nuclear materials, helium-3 targets for tritium production in fission systems, global nuclear material monitoring, sensors for detecting chemical and biological warfare agents, advanced oxidation technologies for chemical demilitarization, advanced nuclear fuel processing and radio-nuclide separations, integrated approaches to advanced machining, improved atmospheric transport in complex terrain, and subsurface directed-energy methods for groundwater treatment.



Materials Science

Fundamental and Applied Studies of Helium Ingrowth in Plutonium

Michael Stevens

The overall objective of this project is to begin development of new tools and techniques for characterizing the effect of radiolytic aging on the properties of weapons-grade plutonium. To accomplish our goal, we must design new techniques for directly measuring helium transport in aged material; develop ion-beam techniques for artificially aging plutonium through combined helium/heavy-ion implantation as well as develop mesoscopic microstructure simulations to predict helium/point defect energetics and segregation tendencies; conduct *ab initio*, total-energy calculations to develop a better understanding about the way in which group IIIB elements stabilize the delta phase; and develop spall codes and techniques for measuring dynamic properties of materials under shock conditions by using the laser-driven miniflyer technique.

The thermal effusion work for measuring helium transport has successfully progressed this year. We now

have a functional system in place for measuring, with high sensitivity, helium release from small plutonium coupons. Experiments will begin this coming year on coupons secured from the Laboratory's Pit Surveillance Program. In the area of "artificial" aging induced by ion-beam implantation, this year we succeeded in using radiation damage codes to simulate alpha-decay damage in plutonium. We selected and synthesized a gold-silver alloy simulant to begin the ion-beam implantation studies. Helium implantation has been successful, but we encountered problems with heavy-ion implantation because, in this case, surface sputtering occurred instead of implantation.

Mesoscopic structure modeling efforts resulted in calculated energies for a variety of defects in delta plutonium, such as certain orientation grain boundaries, faults, and vacancy and interstitial-point defects. Further work showed that certain clusters of five to six vacancies may be energetically

more stable than free vacancies, providing incipient traps for the diffusion of helium. Total-energy calculations have indicated that Pu_3Ga compounds may be the ground-state preferred phase in this system, which suggests that fine-scale precipitation of this phase over time may be possible in aged materials. This year, we have also performed calculations to determine local relaxations around a gallium atom in delta-phase plutonium, and next year we will refine these calculations. Moreover, we have completed measurements of charge densities and potentials for the Pu_3Ga phase. To predict spall in planar (layered) microstructures, we have developed a one-dimensional, finite-difference code that will allow us to study model alloys and, eventually, plutonium. Finally, this year we have designed a special chamber for assessing plutonium films under shock conditions.

Publications

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Cost-Effective Development of Thin Films for Flat-Panel Displays

Joysree Aubrey

We have used an integrated concept-to-prototype process for modeling and fabricating thin films for applications in flat-panel displays. The approach for developing "thin films by design" has proved to be invaluable in materials research. The project included personnel from three divisions at Los Alamos: Applied Theoretical Physics, Materials Science and Technology, and

Theoretical. These personnel worked together to develop thin-film semiconductors and conductors with superior qualities.

We deposited films using a state-of-the-art, flow-through ion gun and characterized the samples with an extensive array of diagnostic equipment. Theoretical support consisted of simulation of the performance of the ion gun, development of adaptive pro-

cess-control methods, and materials and device modeling for the films and their applications.

We reached a number of significant milestones during the course of the project: (1) deposition of oriented films of zinc oxide, indium tin oxide, and silicon; (2) characterization of the films; (3) mesh set-up and simulation of the ion-gun performance using the two-and-one-half dimensional code MERLIN; (4) evaluation of deposition parameters for use in the development of adaptive-control techniques; and (5) initiation of materials and device modeling and development of a device-modeling code, FEDPIX.

Development of High Magnetic Fields for Energy Research

Joe D. Thompson

The goal of this project is to demonstrate the feasibility of building a 100-T magnet for high-magnetic-field research. If successful, this project would enable us to meet a longer-term goal of establishing the technological and scientific bases upon which DOE/Office of Basic Energy Sciences will form a strategic alliance with the National Science Foundation to build a revolutionary 100-T, nondestructive magnet. This magnet will provide high magnetic fields for furthering energy-related science and technology important to the DOE mission. In preparation for the 100-T magnet, we have been developing diagnostics and have begun some high-field materials research measurements at 50 T.

This year we have designed (1) a capacitor bank for a 50-T insert and (2) the signal sequencing patterns to control a 50-T outer magnet of a combined 100-T magnet. We have also made extensive electrical simulations for a variety of 100-T magnet designs.

In parallel with the magnet work, we have used molecular-beam epitaxial growth of GaAs to fabricate large-area, very thin (100-nm thick) cantilevers that can be used for ultrasensitive micromagnetometry from room temperature to 30 mK in arbitrarily high magnetic fields. We have also discovered what appears to be quantum oscillations in the magnetoresistance of "nonmagnetic" YbInCu_4 and evidence for substan-

tially different field dependencies of the charge and spin gaps in Kondo insulators at fields to 50 T. In addition, we have taken high-field thermodynamic and transport measurements of $\text{Ce}_{0.97}\text{La}_{0.03}\text{Pd}_3$ to test theoretical predictions for Kondo-hole behavior.

Publications

Boenig, H.J., L.J. Campbell, K.R. Eberl, et al., "Design Status of the US 100-Tesla Non-Destructive Magnet System" (submitted to *7th International Conference on Megagauss Magnetic Fields*).

Harris, J.G.E., D.D. Awschalom, et al., "Fabrication and Characterization of 100 mm Thick GaAs Cantilevers" (submitted to *Rev. Sci. Instrum.*).

Lawrence, J.M., T. Graf, M.F. Hundley, et al., "Kondo-Hole Behavior in $\text{Ce}_{0.97}\text{La}_{0.03}\text{Pd}_3$," *Phys. Rev. B* **53**, 12559 (1996).

Advancing the Technology Base for High-Temperature Membranes

Robert Dye

This project tackles major issues barring the implementation of high-temperature membranes to separations and catalysis that might have a large impact for the DOE and for industry. Advances made in this project have moved the state-of-the-art toward high-temperature membrane viability and improved overall energy efficiency.

We have accomplished modeling and data analysis of permeation rates through composite metal membranes. The model accounts not only for the well-understood Sievert's law regime but also for the less-understood "surface-effects" regime. In the

Sievert's law regime, permeation rate is controlled by the diffusion of atomic hydrogen through the bulk phase. In the surface-effects regime, permeation rate is controlled by one or more of several mechanisms for transporting gaseous hydrogen, as atomic hydrogen, into the bulk phase. We have been very encouraged by tests of the multimetal membranes in a reformed fuel mixture. Without optimization, the membranes produced a hydrogen flux of 17 standard cm^3/cm^2 at 286°C, with a partial pressure of 0.5 atm of hydrogen across the membrane. After performing a 27-h lifetime test using the gas mixture of

74% hydrogen, 25% carbon dioxide, and 1% carbon monoxide, we found that the membrane still performed well.

We have applied for a patent on the composite metal membrane and have successfully licensed this metal membrane technology to industry.

Publications

Peachey, N.M., R.C. Dye, P.D. Ries, et al., "Pulsed Laser Deposition of Zeolitic Thin Films: Novel Structures for Molecular Recognition," *J. Porous Mater.* **2**, 331 (1996).

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Giant Magnetoresistance Materials for Magnetic Recording Technology

Robert Heffner

This work focused on a class of transition-metal-oxide (TMO) materials (LaMnO_3 doped with calcium, barium, or strontium); these materials exhibit an insulator-to-metal transition near their ferromagnetic phase-transition temperatures. This transition from a paramagnetic insulator to a ferromagnetic metal yields a very large magnetoresistance. Thus, these materials may have important uses as magnetic sensors in a variety of applications, ranging from automobiles to read heads for magnetic storage. Practical use of these materials depends upon learning to control the synthesis parameters (principally temperature, pressure, and composition) to achieve a specific carrier concentration and/or mobility. A second challenge is the high magnetic fields (greater than 1 T) currently required to achieve a large change in resistance. We conceived of two novel approaches to this field-sensitivity problem; these approaches involve developing multilayers of the TMO

materials. We are also exploring the use of epitaxial strain to change the transport properties in thin-film multilayers.

Using thermogravimetric analysis on materials synthesized at different oxygen pressures and temperatures, we have developed a phase diagram for ideal growth conditions. We have studied the effects of lattice substrate epitaxy by depositing $(\text{La,Ca})\text{MnO}_3$ materials on several lattice-matched isostructural substrates: lanthanum aluminate, strontium titanate, and neodymium gallate. X-ray diffraction studies of these films indicate that large amounts of coherent interface strain can be produced. We have successfully adapted a semiconductor strain-layer approach and have fabricated multilayer superlattices by depositing alternating layers of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and strontium titanate perovskites. These stacks exhibit multiple x-ray satellite reflections that are indicative of a highly ordered superlattice structure with a period of

250 Å and d-spacing corresponding to a highly strained material.

Publications

Hawley, M.E., C.D. Adams, P.N. Arendt, et al., "CMR Films' Structure as a Function of Growth and Processing" (to be published in *J. Crystal Growth*).

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Hundley, M.F., J.J. Neumeier, R.H. Heffner, et al., "Transport and Magnetism Correlations in Thin-Film Ferromagnetic Oxides," *J. Appl. Phys.* **79**, 4535 (1996).

Louca, D., E.L. Brosha, and T. Egami, "Observation of Polaronic Lattice Distortion in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ by Pulsed Neutron Diffraction" (submitted to *Phys. Rev. Lett.*).

Louca, D., W. Dmowski, T. Egami, et al., "Evidence of Lattice Polarons in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ by Pulsed Neutron Diffraction" (submitted to *Phys. Rev. Lett.*).

Characterizing Mechanical Effects of Aging Damage

Philip M. Howe

Our goal is to use molecular-level spectroscopic data and theoretical information from atomistic calculations in the parameterization of a micromechanical model designed to assess aging effects on the properties of particle-filled composites. The results will be used in the development of a micromechanics-based constitutive model for such materials. The main emphasis is on Plastic-Bonded Explosive 9501 (PBX-9501) and its constituents, high-melting explosive (HMX) and Estane binder.

During the reporting period, we established shipping arrangements and experimental standard operating procedures to allow studies of explosive materials and made initial spectroscopic measurements for fresh and aged samples of both the pure binder and PBX-9501. Spectra for the fresh and aged samples differed, indicating changes due to aging, and we concluded that spatially resolved data will be required for an improved understanding of the aging behavior. We purchased software for atomistic

studies of polymeric systems and performed preliminary calculations of the elastic constants for the amorphous component of Estane; calculations for pure HMX are also underway. We will extend these studies to provide estimates of the adhesion strength between the HMX and binder.

We computed micromechanics-based stress-strain curves as a function of "binder" concentration for a model composite system that crudely mimics an explosive formulation. We predicted reasonable behavior and are making refinements. Finally, we incorporated advances in a constitutive theory for particle-filled composites into a computer model and predicted much of the known characteristic behavior.

High-Magnetic-Field Research Collaborations

Johndale Solem

The purpose of this project is to exploit the research potential of the pulsed magnetic fields that might be possible with PEGASUS and explosive-driven flux-compression generator sources to explore completely novel ideas in condensed-matter physics and chemistry. The project links the Laboratory to the academic and industrial communities by involving those communities in our research programs, which enhances the technical vitality of the Laboratory, benefits the broader scientific community, and creates a broader constituency for science-based stockpile stewardship.

The initiative brought together American, Russian, Australian, and Japanese researchers from around the world. We started with a campaign of experiments (Dirac series) using high-explosive-driven flux-compression generators. The Dirac series included four ~150-T experiments using a linear explosive-driven flux-compression generator designed at Los Alamos and three ~1000-T experiments using a cylindrically imploding, explosive-driven flux-compression generator designed at Arzamas-16.

Our experiments explored quantum limit phenomena in two- and three-dimensional organic metals, semi-metals, transition metals, and electron gases; chemical-bond manipulation; and nonlinear Faraday rotation. These experiments have been described in detail by other documents on the LDRD program. We are still analyzing much of the data.

Publications

Brooks, J., et al., "Quest for the Quantum Limit in Three Dimensional Metals" (Seventh International Conference on Megagauss Magnetic Field Generation and Related Topics, Sarov [Arzamas-16], Russia, August 5-10, 1996).

Clark, R., et al., "The Extreme Quantum Limit of Dilute 3D Electron Systems: Experimental Probe of Transport in Semiconductors and Semimetals to 500 Tesla" (Seventh International Conference on Megagauss Magnetic Field Generation and Related Topics, Sarov [Arzamas-16], Russia, August 5-10, 1996).

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Solem, J., and M. Sheppard, "Experimental Quantum Chemistry at Ultrahigh Magnetic Fields: Some Opportunities" (submitted to *Int. J. Quantum Chem.*).

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Ceramic/Polymer, Functionally Graded Material (FGM), Lightweight Armor System

John Petrovic

Significant improvement in body armor has been listed as one of the Department of Defense's (DoD's) "Top Ten Tough Problems." Required advances in lightweight body armor to meet the DoD's needs can no longer be met through incremental advances in post-Vietnam-era armor systems based on Kevlar-type fabric vests and will require the incorporation of lightweight ceramics. The approach that provides the most opportunity for improvement in performance is to employ FGMs in which the surface intercepting the bullet is made of a very hard ceramic that can break up the bullet. This ceramic is then graded into an energy-absorbing polymer or metal to absorb energy and bullet fragments.

The critical step for developing ceramic/polymer FGM armor is developing a graded-porosity, boron carbide (B_4C) ceramic that can then be liquid-infiltrated with a polymer material or a metal such as aluminum. We have focused our efforts on developing a graded-porosity, B_4C ceramic. Because we have chosen the B_4C/Al system as a benchmark to gauge the performance of the B_4C /polymer armor, our secondary focus has been on establishing procedures for infiltrating aluminum into the B_4C ceramic. We have established that gradients in carbon-induced B_4C densification and gradients in particle-size distribution are the two most promising approaches for developing FGM armor.

New Anion-Exchange Polymers for Improved Separations in Nuclear and Industrial Applications

Gordon Jarvinen

The objective of this work is to improve our understanding of how the structure of a new class of anion-exchange polymers controls the binding of anionic actinide complexes from solution. This kind of fundamental data is needed to develop practical separation systems that will reduce the cost of actinide-processing operations within the DOE complex. These systems will separate actinides from both process and waste solutions. In addition, anion exchange is widely used in industry, and these new materials may have much broader applications in areas such as water treatment, pollution-control technology, and purification of chemical products.

We designed and synthesized several new series of bifunctional, anion-exchange polymers, and we tested their ability to remove three actinides—plutonium(IV), americium(III), and uranium(VI)—from nitric acid. The polymers contain a pyridinium site derived from the host poly(4-vinylpyridine) and a second cationic site (either trimethylammonium, pyridinium, or trimethylphosphonium) attached through a chain of two to six methylene groups. The new polymers removed plutonium 4–10 times more efficiently than can the best commercial materials presently available. The sorption kinetics and distribution coefficients for plutonium(IV) were generally best when the two cationic sites were

separated by a five-methylene spacer. The order of affinity for plutonium from 7-M nitric acid was pyridinium > trimethylphosphonium > trimethylammonium. Replacing the central methylene group in a five-unit spacer with an ether oxygen further enhanced the sorption of plutonium. Compared with other separation techniques, our new polymers offer the prospect of removing plutonium more effectively from many nitrate process and waste solutions while decreasing the volume of secondary waste generated.

Publications

Marsh, S.F., G.D. Jarvinen, and R.A. Bartsch, "New Bifunctional Anion Exchange Resins for Nuclear Waste Treatment" (to be published in *React. Polym.*).

Engineering and Base Technologies

Detection of Underground Structures and Tunnels

Joseph Mack

The primary objective of this project is to assess electromagnetic (EM) and gravitational methods for detecting underground structures. We also considered methods for detecting land mines and improving underground communications.

Using an improved means of electromagnetic scattering, we obtained excellent agreement between our theoretical predictions and experimental results when sensing a grounded #14-gauge wire buried 10 m. We also were able to detect the presence of an ~30-m-deep, 7.3-m-diameter, conductor-carrying tunnel. We performed these experiments at Sandia National Laboratories, New Mexico,

and the Nevada Test Site (NTS), respectively.

It is believed that underground communications using low-frequency EM waves coupled to any longitudinal conductor propagate as a surface guided wave with no cutoff frequency. We successfully demonstrated this hypothesis at ~300-m depths at the Lyner Facility at the NTS.

We have used resonant microstrip-patch antennas to detect and image antipersonnel mine mockups in both dry and wet soil, and we also established clutter sensitivities.

In addition, emphasizing quasi-analytic techniques, we developed a computer code to model EM detection

of deeply buried tunnels. We have successfully modeled critical aspects of tunnel detection.

Through another buried-wire experiment in which we used low-temperature superconducting quantum interference devices (SQUIDs), we determined that more design and hardware development is necessary for successful gravity-gradiometry detection of underground structures. High-temperature SQUIDs show new promise as this new technology becomes interlaced with noise-control electronics.

We assessed other tunnel-detection technologies in conjunction with the experiments performed by other institutions. Of note was detecting tunnel presence with a magnetometer mounted on the unmanned, airborne CYPHER vehicle, which was flown over the Yucca Mountain tunnel (7.3-m diameter, ~30 m below the surface).

Active Noise and Vibration Control for Vehicular Applications

Paul Lewis

In this project we planned to develop a benchtop demonstration of a semiactive suspension system based on real-time nonlinear control of a magneto-rheological (MR) shock absorber. We embarked on this project because of the Laboratory's interactions with General Motors (GM) Delphi in the area of active noise and vibration control and because of the Defense Advanced Research Project Agency's (DARPA's) interest in MR technology for military applications.

We carried out background research and a literature search on semiactive suspensions and controllable shock absorbers, and we developed and adapted numerical models and simulations of alternative nonlinear control algorithms for use with an MR shock. (In an MR shock, friction is controlled rather than dampened.) We specified and assembled the control system consisting of a 486-based personal computer (PC) that has a special-purpose digital signal-processing board (TMS320C31) to handle the control

loop. We designed a mechanical demonstration fixture to hold the damper/spring assembly, and we specified and procured a custom-made MR shock from MR Technologies. (MR shocks are still a developing technology and are not readily available.) To characterize the performance of the MR shock, we took measurements, which were satisfactory. However, the device leaked MR fluid and had to be repaired by MR Technologies; it subsequently began to leak again.

Because interests at both GM and DARPA changed, we did not implement the benchtop demonstration design. However, we have documented the design, simulation, and measurements in the project's final report.

Study of Possible Detector Geometries for Detection of Radioactivity in Moving Vehicles

Robbie York

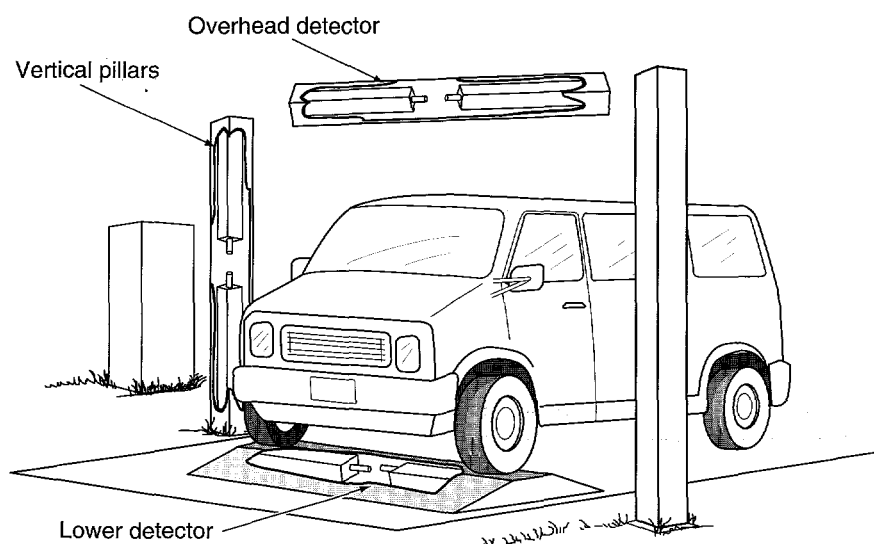
The security plans for many DOE facilities require monitoring of pedestrians and vehicles to control the movement of special nuclear material (SNM). Vehicle monitors often provide the outermost barrier against the theft of SNM. The standard SNM vehicle monitors consist of two pillars that the vehicles drive through. The two pillars contain both large plastic

scintillators and decision-making electronics. These automatic monitors determine the presence of SNM by comparing the gamma-ray and neutron intensities of the occupied vehicle monitor to the background radiation level of the unoccupied monitor.

The sensitivity of these monitors varies for different types of vehicles

and depends on the size, spacing, and number of detectors in the monitor. For a given detector configuration and vehicle, two of the dominant sensitivity factors are the occupancy background suppression and the shielding provided by the components of the vehicle. The goal of this project is to evaluate different detector configurations as a means of improving the sensitivity of these instruments to achieve a vehicle monitor that is economical, practical to install, and sensitive enough to be an effective barrier to illegal transportation of SNM.

The most severe shielding locations in a vehicle are between the door posts, above the engine block, and below the engine. By placing detectors above and below the vehicle (see figure), we minimized variations in the sensitivity caused by gamma-ray shielding. With the source between the two door posts, the sensitivity of the side detectors was very poor, but the sensitivity of the lower detector was high. However, with the source above the engine block, the situation was reversed. We found that adding the overhead detector did not increase the worst-case sensitivity. Summing the count rates of the side and lower detectors decreased the minimum detectable mass by a factor of 3. However, when we summed all three detector groups, the sensitivity improved by a factor of 5, while the nuisance-alarm rate remained constant.



A sketch showing the configuration of the four-pillar detector that we tested.

Environmentally Conscious Coal Combustion: Development of Process Monitors and Improved Numerical Models

Donald D. Hickmott

Many inhabitants on the Navajo reservation use free subbituminous coal in home-scale coal stoves for their home heating. Coal is used for similar small-scale combustion in many developing nations, particularly China. The principal coal-combustion

need on the Navajo reservation, and potentially in the developing world, is for a high-efficiency, smokeless stove that burns diverse feedstocks (i.e., coal, wood, biomass). In this project we evaluated the contaminants produced during coal combustion in a Navajo home-scale coal stove and the

possible engineered controls on those contaminants.

Unlike utility-boiler combustion, home-coal combustion emits contaminants cyclically. Only low levels of sulfur dioxide and other contaminants are produced, but they are potentially high enough to exceed Environmental Protection Agency standards for ambient air because of winter atmospheric inversions that occur in the neighboring town of Shiprock, New Mexico. We evaluated several engineering controls on home-coal-stove emissions, such as small-scale scrubber systems and improved-efficiency stoves.

Establishing the Operational Durability of Polymer Light-Emitting Diodes

Ian Campbell

Recently discovered polymer light-emitting diodes (PLEDs) have the potential to revolutionize display technology for defense and civilian applications. Displays are expected to be major drivers in both the computer and the high-definition television industries in the near future. At Los Alamos we are collaborating with Hewlett-Packard Company, Unix Corporation, the University of Texas at Dallas, and the University of California at Santa Barbara to develop PLED technology.

Our ongoing collaborative research program has made it clear that PLEDs

have all the device attributes (efficiency, emission colors, and operating voltage) required to build a successful display technology. We initiated this project to establish meaningful device operating lifetimes and to understand PLED failure mechanisms with the goal of controlling device reliability and ultimately producing a viable commercial product.

We established a PLED lifetime testing facility to measure the change in PLED light output and drive voltage at constant current bias as a function of time for different current bias levels, operating temperatures, and

device (polymer) thicknesses. We have identified that the dominant failure mechanism of the PLEDs is delamination of the electron-injecting metal contact, which occurs at less than 1000 hours of operation. This year we developed a new electro-absorption technique to measure the electric field distribution inside the PLEDs. We used this technique to assess relative device reliability.

Publications

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Helium-3 Targets for Tritium Production in Fission Systems

Brian James

Neutron irradiation of ^3He is a potentially attractive method for producing tritium. Should this method be implemented, experimental, defense, and power reactors could provide a contingency supply of tritium. However, the safety of putting ^3He in a reactor has always been questioned—the loss of ^3He would result in increased reactivity. Moreover, containment of the tritium produced is a concern under both normal operating and accident conditions. The objective of our project is to develop innovative designs of reactor targets for producing tritium by neutron irradiation of ^3He . The new targets should overcome

the technical problems associated with tritium production.

We have invented a target that reduces or eliminates the additional reactivity resulting from a loss of ^3He ; this target makes the use of ^3He in reactors a viable option for supplemental or contingency production of tritium. In the inherently safe target (IST), ^3He normally "cloaks" an additional strong solid absorber such as boron-10. If the ^3He gas should leak out of the target canister, the reactor flux will immediately "see" the solid absorber. The target canister can be designed so that the reactivity shift on a loss of ^3He is negligible or negative.

The special target design is an engineered, passive safety feature.

Our new concept for a reactor target was successfully tested in the solution high-energy burst assembly at Los Alamos. Targets of the type we designed could be used for supplemental or contingency tritium production in existing DOE reactors—the advanced test reactor (ATR) at the Idaho National Engineering Laboratory and the Fast Flux Test Facility (FFTF) at the Hanford Site—or in commercial light-water reactors. ISTs could also be used in flowing ^3He systems at FFTF and ATR with on-line tritium extraction that allows continuous removal of tritium from ^3He and thus lessens containment problems. Such use would greatly reduce the inventory of tritium at risk, and it would significantly reduce permeation of tritium into the reactor coolant. Finally, it would also simplify shipment of tritium for use at Savannah River.

Explosives Detector Using the Optical Signature of Deflagrating Explosive Particulates

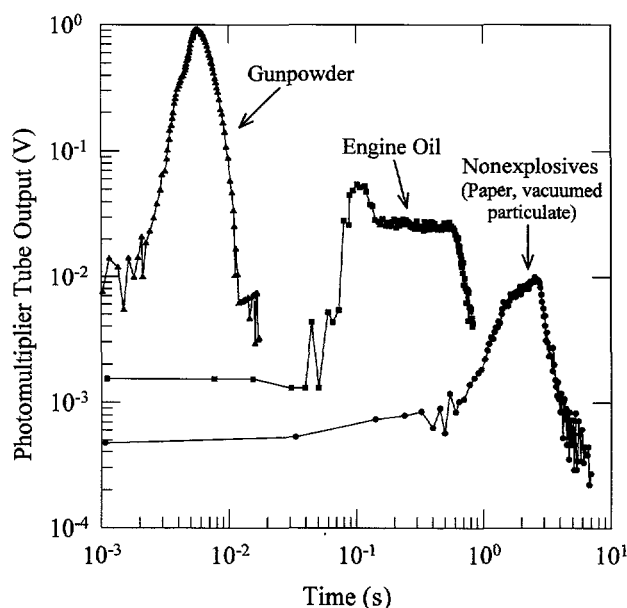
Herbert O. Funsten

Because of the stickiness of explosives, surfaces coming in contact with an explosive will become contaminated with explosive particulates. These particulates, which will exist in possibly large amounts on the explosive packaging and environs, provide an important avenue for detecting the presence of explosives.

In the past year, we developed a unique technique for detecting explosives residue. This technique detects the rapid burn of explosives, which have a higher oxygen content and a more rapid breakup of molecules in comparison with nonexplosives. The detection apparatus consists of (1) a sample surface, (2) a heat source that initiates deflagration, (3) a photomultiplier tube that detects the optical signature resulting from deflagration, and (4) a signal analyzer. Our tests of the explosives detector show that the light output from the burning residue of explosives is rapid and intense, which contrasts with the emberlike burn of nonexplosives.

The accompanying figure shows pulse signatures from 5- μ g gunpowder particulates (used in 45% of bombs and devices used or confiscated in the United States), engine oil, and nonexplosive particulates such as paper and

household dust. The optical signature from the gunpowder is short and intense, whereas the signatures from the engine oil and nonexplosives are dim and long. Since the pulse magnitude and width are anticorrelated, the ratio of the magnitude to the width enables a simple but extremely sensitive technique for differentiating explosives from nonexplosives. Advantages of this detection technology include fewer false-alarm rates, faster sample analysis, less costly instrumentation, and higher sensitivity.



A comparison of the optical output from explosive and nonexplosive materials.

Directed-Light Fabrication—A Laser Metal-Deposition Process for Fabrication of Near-Net-Shape Components

Gary Lewis

Directed-Light Fabrication (DLF) is a direct metal-deposition process developed at Los Alamos National Laboratory and is a revolution in manufacturing technology. The DLF process is the first rapid-prototyping, free-form fabrication process that deposits metals directly to near net shape. It is a material-independent process capable of processing any

powder material that can be melted. Our studies proved feasibility with any metal that can be made into powder form and with intermetallic compounds.

Our assembly work on a five-axis DLF machine in this project was an extension of earlier efforts that had been limited to the three-axis DLF manufacture. The transition to the

five-axis capability allows true three-dimensional replication of metal components as designed on a computer; by contrast, the three-axis machine is capable of only two and one-half dimensions.

During the year we succeeded in assembling and testing the five-axis system, including assembly and test of a support structure and powder-feed apparatus. The system has four powder feeders that can be run individually or simultaneously to provide materials to the focal zone of the laser, where they are fused into the desired component. This accomplishment is a significant advance in capability.

Modeling and Assessment of Concrete and the Energy Infrastructure

George Guthrie

Concrete is an essential component of our energy infrastructure. It is the primary material used by the energy and transportation sectors (for example, in roads, bridges, runways, dams, reactor containment vessels, and radioactive- and metal-waste-disposal). The strength and durability of concrete, which are the properties that determine its effectiveness in any of these applications, result from chemical and structural changes that occur during the minutes to years that follow the pouring of a particular concrete structure. These chemical and structural changes are controlled by a variety of geochemical and mineralogical processes that also occur in some geological environments.

The experimental and modeling capabilities that we developed for geological systems such as Yucca Mountain are useful in our work to improve the design of next-generation concrete. Our first goal is to understand the geochemical processes that lead to the alkali-silica reaction (ASR), which is one of the main impediments to durable concrete worldwide. ASR is an interaction between alkalis in the fluid and some silica-rich components of the aggregate. It results in the formation of a gel that causes the concrete to fracture, greatly reducing the concrete's strength and longevity.

As part of our scoping activities, we produced an inexpensive and environmentally friendly set of stains that can detect deleterious reaction products associated with ASR. This method is in contrast to the one currently used by highway departments, which is based on uranyl acetate. The uranyl acetate method produces uranium-contaminated wastes, exposes personnel unnecessarily to radioactivity, is difficult to use, and may result in ambiguous information about the nature of ASR in a particular concrete. We also obtained promising results when we used nonlinear resonance ultrasound spectroscopy to evaluate fractures in concrete.

We are developing this work in conjunction with the Alliance for Transportation Research, which recently assembled a national expert panel that conducted a successful independent, external review of our efforts.

Global Nuclear Material Monitoring

Jo Ann Howell

To facilitate the development of the nuclear material monitoring system of the future, we are working to design a detailed plan for advanced integrated facility monitoring. We will identify the necessary components, the appropriate demonstration facility, and the enabling technologies.

We identified the following major components: material-tracking sensor systems, personnel-tracking sensor systems, information management systems, measurement systems to perform assay, analysis tools to process the collected data, and software to tie all of the above functions together into one system.

We have identified several necessary technologies. Some of those that presently exist include interface building, visualization, authentication,

pattern recognition, radiation sensor design, portal monitor sensor design, digital video production, and facility simulation. Some of the technologies that we still need to develop include anomaly detection for particular safeguards applications; integration of databases with analysis systems, alarm systems, and displays; and design and implementation of smart sensors, data-mining tools, and reconciliation tools.

We have initiated a publication series about Los Alamos global nuclear-material-monitoring projects. The first document to be produced in the series will be about monitoring at the Japanese facility, Monju. We have identified simulation as an area that is not often exploited in facility monitoring systems. Facility simulations can

be run in parallel with actual facility operations to improve the capability for detecting departures from standard operating conditions. We also enhanced the computerized Local Area Network Material Accounting System (LANMAS) to incorporate access control and authorization.

Publications

Howell, J.A., "Analysis of Facility-Monitoring Data" (to be published in *Nucl. Mater. Manage.*).

Howell, J.A., H.O. Menlove, P.E. Argo, et al., "Global Nuclear Material Monitoring with NDA and C/S Data through International Facility Monitoring" (to be published in *Nucl. Mater. Manage.*).

Proceedings of *The Facility Monitoring Workshop*, J.A. Howell, Ed., Los Alamos, N. Mex., September 19-21, 1995, Los Alamos National Laboratory document LA-CP-95-251.

Frequency-Resolved Optical Gating: A Diagnostic for the Characterization of Optoelectronic Materials and Devices

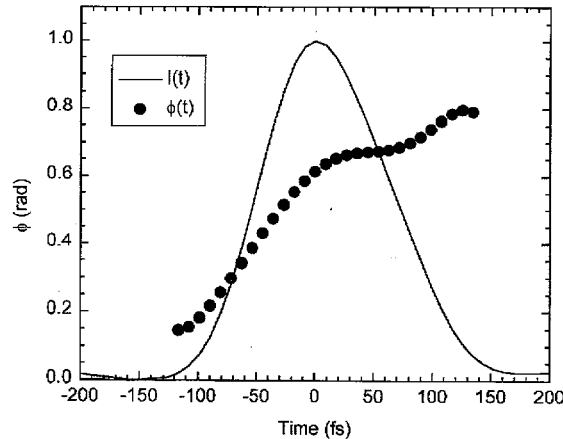
Antoinette Taylor

Frequency-resolved optical gating (FROG) is an ultrafast diagnostic technique that measures the full electric field, both instantaneous amplitude and phase, of an arbitrary ultrashort pulse. Because FROG is a general, broad-band optical diagnostic, it can be used in research areas for which characterizing the full electric field of an optical pulse would provide critical insight into physical processes. One area in which FROG could have an enormous impact is in understanding the coherent interaction between optical pulses and optoelectronic materials and devices. The objective of this research is to address issues relevant to high-speed optoelectronic materials and devices using FROG.

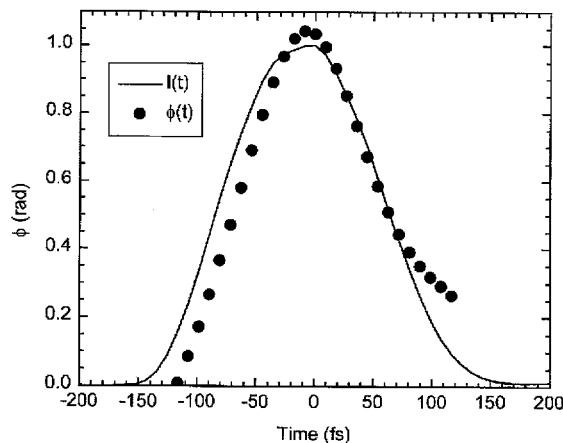
We have demonstrated FROG as a technique to determine basic properties of optical materials such as dispersion, nonlinear refraction, two-photon absorption, and cross-phase modulation by measuring the phase change of the optical pulse with FROG after the pulse traverses the material. The emphasis of this research is to determine the types and accuracy of measurements possible with FROG. We have completed a thorough set of measurements of the nonlinear index, n_2 , in a variety of optical materials using FROG. The accompanying three figures exhibit typical intensity and phase data derived from the FROG spectrograms used to determine n_2 . We have demonstrated that FROG accurately measures n_2 in optical materials, with the error dominated by the uncertainty in the fluence measurement. We are currently completing a second set of measurements on cross-phase modulation in optical materials.

Publications

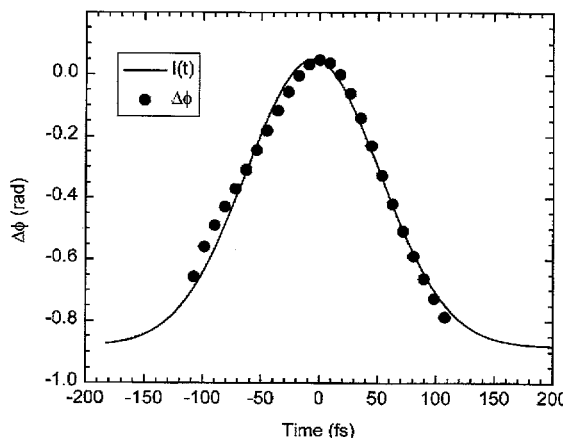
Taylor, A.J., G. Rodriguez, and T.S. Clement, "Determination of the n_2 through Direct Measurement of the Optical Phase," *Opt. Lett.* **21**, 1812 (1996).



Normalized intensity and phase for a pulse with no sample in the beam. The pulse width is 130 fs. The phase (ϕ) varies almost linearly with time over the pulse and hence represents a nearly transform-limited pulse.



Normalized intensity and phase of the pulse after it traverses 0.95 cm of fused silica (Corning 7940), with a peak intensity of 5.2×10^{10} W/cm². The phase follows the intensity envelope, indicating the presence of significant self-phase modulation due to the n_2 interaction in the sample.



Phase change— $\Delta\phi(t)$ —is plotted for this data along with a fit (solid line) that involves simply scaling the measured normalized temporal intensity profile to fit $\Delta\phi(t)$. (To obtain $\Delta\phi(t)$, the calculated value for linear dispersion in the sample is added to the phase data with no sample present before subtracting the phases measured with and without the sample in the beam.) This fit yields a constant that is proportional to $\Delta\phi(t)/I(t)$ and from which n_2 can be determined. This set of data yields $n_2 = 2.45 \times 10^{-16}$ cm²/W for fused silica at 804 nm.

Neutron-Based, Land-Mine Detection System Development

Thomas McDonald

The goal of this project was to examine the feasibility of developing a buried land-mine detection system by detecting and analyzing prompt gamma-rays induced by neutron interrogation. This is a mature concept; however, it has not been successfully applied to the buried-mine detection problem because of lack of both a suitable neutron source and a detection system having a sufficiently high signal-to-noise ratio. Most studies indicate that a source strength in the range of 10^9 – 10^{11} n/s would be necessary to achieve a reliable detection capability requiring interrogation times of only a few seconds.

We considered two neutron sources that have the potential of neutron fluxes in the neighborhood of 10^{11} n/s: the inertial electrostatic confinement source (see schematic

diagram below) and the intense ion-beam source (see schematic diagram on p. 26). The advantage of these sources is that they can be turned off when not in use and can be used over a wide range of operating modes from steady state to pulsed. We also reviewed alternative detection techniques and carried out preliminary measurements using mock high-explosive material.

We found that the primary advantage of the neutron-based detection approach for nonmetallic mines is that the approach is a powerful discriminator. Other approaches, such as ground-penetrating radar and infrared detection, can detect buried objects; however, these objects may or may not be mines. The neutron-based approach, on the other hand, detects explosives and differentiates between

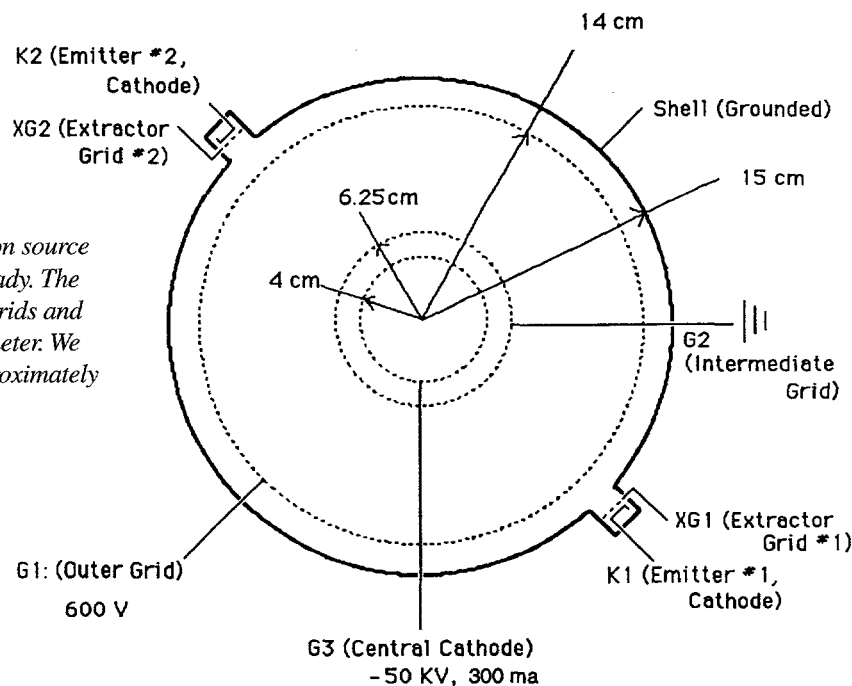
inert objects and explosive-containing mines. Our approach of using a controlled, high-flux neutron source increases the speed of detection and allows a longer standoff distance. A vehicle is still needed to transport the system, and we project that costs will be relatively high compared with costs of metal-detection techniques currently in use. We believe that the neutron-based approach can be used most effectively in conjunction with other approaches in a suite of complementary detection sensors.

Publications

Davis, H.A., G.E. Remnev, et al., "Intense Ion Beam Treatment of Materials," *Bull. Mater. Res. Soc.* **21** (8), 58 (1996).

Davis, H.A., J.C. Olson, W.A. Reass, et al., "Progress Toward a Micro-second Duration, Repetitive, Intense Ion Beam for Active Spectroscopic Measurements on ITER," *Rev. Sci. Instrum.* **68**, 332 (1996).

Schematic of an inertial electrostatic neutron source design for supplying 10^{11} n/s, pulsed or steady. The design is a series of spherical, concentric grids and an outer shell approximately 30 cm in diameter. We estimate the power requirements to be approximately 20 kW.



Development of the Transient-Reactor Analysis Code (TRAC) for Real-Time Applications

G. Niederauer

Traditionally, nuclear-plant training simulators have employed simple thermal-hydraulics codes because of the demands to run in real time and with limited computing power. There has always been a desire to increase the flexibility of such training systems and to increase the fidelity of models in the simulators. Although TRAC is the most advanced code for such applications, many issues need to be addressed to take such a complex code from a batch engineering environment to real-time environments.

The object of this project was to investigate the feasibility of using TRAC in a simulator.

We have worked extensively with GSE Systems, Inc. to write an informal discussion paper on the real-time applications of TRAC. Together we outlined technical issues relating to taking a batch code into real time and a staged approach for developing what we would call TRAC-RT, starting with a proof of concept. Los Alamos provided the expertise on

TRAC, while GSE provided the expertise on real-time systems. Discussions then expanded to (1) real-time software design techniques to integrate TRAC into a real-time simulator and (2) ways to modify engineering plant models for use in a simulator.

We also worked on the so-called Robinson plant model, modified it for simulator use, and ran several transients cases to characterize TRAC's performance in real time. We identified areas where run-time could be improved and explored means for modifying TRAC to achieve such improvement. We investigated interfaces between TRAC and a real-time system, including data structures, graphical user interfaces, and real-time executive control.

Rapid Prototyping of Hazardous Materials Using the Directed-Light Fabrication Process

Gary Lewis

In the past, fabricating components from hazardous materials such as beryllium has been difficult and expensive because of both the number of processing steps necessary to get from the raw material to the finished product and the controls necessary to process the materials safely without contaminating the environment. Now, however, the directed-light fabrication (DLF) process that we developed at Los Alamos can produce, in a single step, near-net-shape (within a few thousandths of an inch) metal components that are fully dense. The process is nearly waste-free, and it eliminates or contains all contaminants produced with conventional methods.

DLF uses tool paths generated from digitally designed solid models to accurately trace the cross section of a

part with a laser beam that melts metal powder particles entering the focal zone. Upon solidification, the metal forms a deposit representing a planar cross section of the part. Multiple cross-sectional layers are formed in succession until the part is complete. The DLF system we currently use has five axes of motion, allowing us to fabricate three-dimensional components and to deliver up to four different powders at the same time or in succession. DLF can be used for depositing any metal or intermetallic compound.

The goal of this project has been to apply DLF technology to fabricate fully dense beryllium components (that is, beryllium components having full theoretical strength). To reduce costs, we modeled the process using

steel as a surrogate, with the intent of applying the knowledge gained from the steel modeling and deposition experiments to fabricating a beryllium component. We anticipate that it will be straightforward to assemble a special system with the necessary engineered controls for handling beryllium or other hazardous materials.

Using DLF process parameters and information about the physical properties of stainless steel as input to a heat-flow code, we modeled finite heat flow in steel. Unfortunately, because we did not have a complete set of beryllium thermophysical properties, we were unable to apply the model to a beryllium component for comparison. From the steel models, we determined that we could control the thickness of the deposited layers if we used heat-flow gradients to help optimize the DLF process parameters. We will correlate the theoretical data from these models with experimental results and will eventually incorporate the data into control loops for real-time process control.

Reactor-Based Tritium Production

Michael Houts

Los Alamos National Laboratory is responsible for stockpile stewardship. As part of its stockpile stewardship responsibilities, Los Alamos must assure that the United States has an adequate supply of tritium for defense purposes. In that context, the goal of our project was to evaluate options for producing reactor-based tritium. Much of our effort focused on evaluating the Fast Flux Test Facility (FFTF). We selected the FFTF because little independent work had

been done related to that option, and it has the potential for providing significant amounts of defense-related tritium.

A major accomplishment of the project was our development of an inherently safe ^3He -based tritium production target designed for use in fast-spectrum reactors (such as the FFTF). Although the basic operating premise is the same, the target is significantly different from the inherently safe targets we had previously

designed for thermal-spectrum reactors. We are currently applying for patents for both the fast-spectrum target and the thermal-spectrum target.

In addition, we assessed all aspects of the tritium production cycle, from target fabrication to extraction of tritium to getting the tritium into the form required by the Department of Defense. The use of flowing ^3He loops (for which FFTF is well suited) could greatly reduce the cost of processing and shipping targets. The use of static ^3He targets rather than flowing ^3He would also reduce costs. If the option for FFTF tritium production is funded, Los Alamos is in an excellent technical position to participate in numerous aspects of this option.

Methods for the Rapid On-Line Detection of Biological and Chemical Weapons

Philip Hemberger

Our objective is to develop technology for the detection (using surrogates) of chemical and biological warfare agents. The project consists of three tasks: (1) to modify a transportable mass spectrometer for the detection of chemical agents; (2) to demonstrate the detection of specific bacterial DNA sequences using a fluorescence-based, single-copy gene detector; and (3) to upgrade a surface-acoustic-wave measurement station.

In the past year, we modified an existing transportable mass spectrometer for the field detection of chemical warfare (CW) agents. The detection technology is based on the combination of membrane sampling and ion-

trap mass spectrometry. We installed a membrane interface on the transportable mass spectrometer and adapted the instrument for the detection of surrogates of chemical warfare agents. The instrument and sampling system are mounted in a 20-in. $\times$ 20-in. $\times$ 36-in. transportable container. The instrument also requires a small cylinder of helium and a rotary vacuum pump, which are mounted externally on the container. We also developed preliminary methods for detecting CW surrogates. The surrogates included chlorobenzene, cyclohexanol, dimethyl methyl phosphonate, and dimethyl sulfoxide. These compounds were detected at approximately

100 ppb by volume in air. The detection of these compounds satisfied the deliverable of demonstrating the instrument for the detection of CW surrogates.

In addition, we developed a technique for the rapid, direct detection—with high sensitivity and specificity—of pathogenic DNA. The method consists of adding two DNA probes to a sample containing the target DNA. The sample is then analyzed by a laser-based, ultra-sensitive fluorescence system capable of detecting single molecules at two different wavelengths. If the target is present, the two probes will bind to it, and their signals will appear simultaneously in time and space. Using the system, we detected single copies of a specific DNA sequence from *Bacillus anthracis* with a signal-to-noise ratio of 20 in only 400 s in an excess of unrelated DNA material.

Night-Vision Device Technology Development

Herbert O. Funsten

The U.S. military extensively uses night-vision devices that utilize image-intensification tubes. These tubes have two significant problems that can critically compromise their operation: (1) the field of view is restricted due to aberrations introduced by the flat-image plane and, (2) light-sensitivity (gain) loss occurs when a bright-light source lies within the field of view. A wide field of view is critical to aviators who need peripheral vision for motion cues and detection of nearby obstacles, obstructions, or

aircraft. Bright-spot suppression is crucial to night missions in an urban or other well-lighted environment (one with streetlights, flares, headlights).

In this project we are developing technology to overcome these problems. First we are designing a curved-image plane, using recently developed detector technology that enables a wide field of view. We have performed optic and electro-optical simulations to allow up to 80 degrees field

of view. For the bright-spot suppression, we have designed a segmented microchannel-plate scheme that suppresses the gain in only that segment illuminated by a bright light source, while it retains full gain across all other segments. In this way, dim objects within the field of view remain visible.

We finished a design and procured an experimental, curved-microchannel-plate tube based on the wide-angle work in the first year. Currently we are waiting for delivery of the fabricated tube. We also finished a prototype for a segmented microchannel-plate design and now are planning a laboratory demonstration of the concept.

Integrated Approach to Advanced Machining

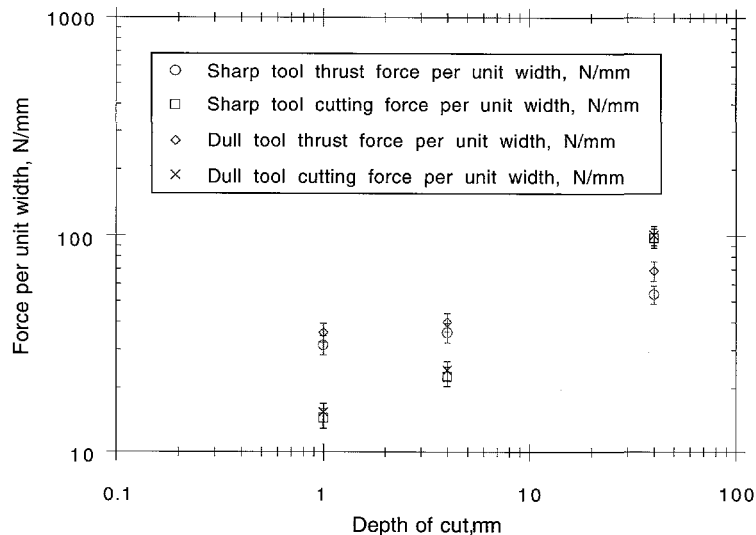
Robert D. Day

The goal of this project was to measure the residual stresses induced by machining as a function of the depth of cut and the cutting tool's sharpness. The sample for these experiments consisted of a titanium alloy that contained 6% aluminum and 4% vanadium. We performed cutting tests on this sample in the as-received condition and after a stress-relieving heat treatment. The first figure shows cutting and thrust forces

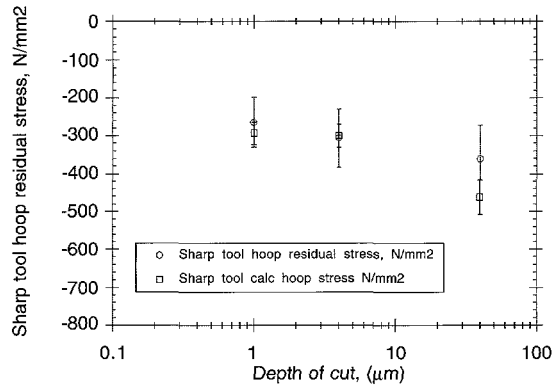
for Ti-6Al-4V specimens. Kennametal donated tools (both dull and sharp) for this project. We measured the tools' sharpness radii at Los Alamos before machining, using interferometry, and determined them to be nominally 1 μm for the sharp tools and 10 μm for the dull tools.

We measured the residual stresses induced by x-ray diffraction using the rotating anode located at the Los

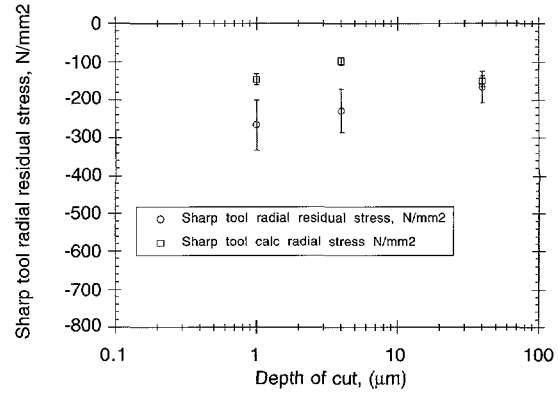
Alamos Neutron Scattering Center. These measurements revealed that the hoop stress increased with depth of cut; however, the radial stress decreased with depth of cut. An elastic-plastic model provided a possible explanation for this behavior. For small depths of cut, the tool makes multiple passes through the damaged subsurface layer, which causes both residual stress components to increase; however, the radial stress increases by a much greater amount than the hoop stress. The second figure compares the calculated residual stress with the measured values.



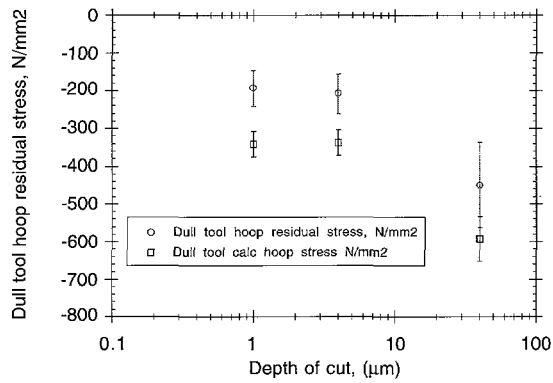
Cutting and thrust forces for heat-treated Ti-6Al-4V specimens. The average is plotted. The uncertainty bars indicate the maximum and minimum measured force values.



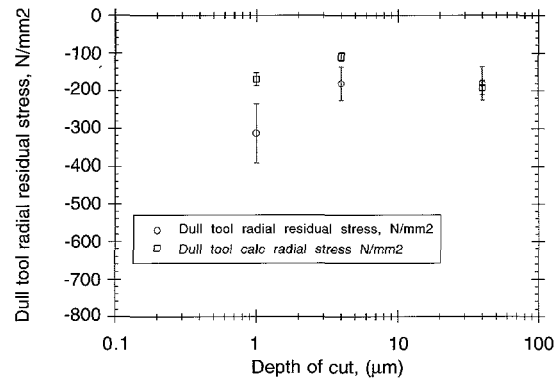
a)



b)



c)



d)

Measured and calculated residual stresses. The average value is plotted. The uncertainty bars for the measured residual stresses are the combination of the variation in the measurements at four locations around each ring and the measurement uncertainty. The uncertainty bars for the calculated values come from the variation in the force measurements that were used in the data analyses: (a) sharp tool hoop stress, (b) sharp tool radial stress, (c) dull tool hoop stress, (d) dull tool radial stress.

Plasmas, Fluids, and Particle Beams

Subsurface, Directed-Energy Methods for Groundwater Treatment

John Coogan

A critical issue in pump-and-treat approaches to groundwater remediation is the limited mass transport of subsurface organics, especially dense nonaqueous-phase liquids (DNAPLs). We are evaluating a novel concept using acoustic waves to enhance the transport and extraction of subsurface organics from leaking underground storage tanks. Until now the majority of research in this area has been focused on improving production in declining oil and gas reservoirs, and the underlying physical mechanisms for enhanced transport have not been thoroughly investigated.

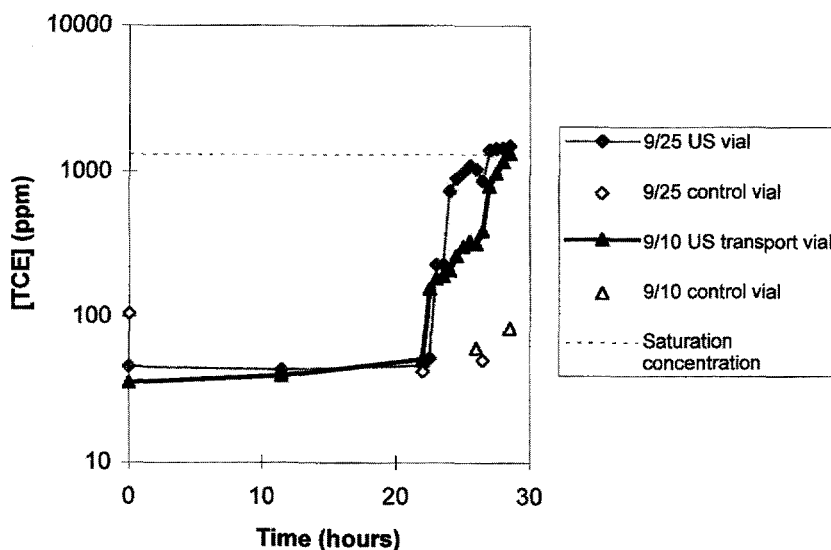
During the reporting period we explored two research paths. First we demonstrated that acoustic energy can enhance the solubility of DNAPLs, specifically trichloroethylene (TCE), in both sand and Pajarito tuff. Experimental work has clearly shown that the proposed process is real (see figure), with removal efficiencies increased by orders of magnitude in both static and flowing systems. This work also suggests several potential mechanisms for the effect. Second, we used cavitation and the resulting sonochemical reactions produced at

higher ultrasound intensities to destroy DNAPL surrogates in sand and soil. Although we discovered that soil can act as a reaction fluidized bed, greatly enhancing sonochemical

reaction rates over those found in simple fluids, the scaling to subsurface remediation is not promising, and the work will not continue.

For the next fiscal year, we will extend the research in enhanced transport under more controlled laboratory conditions to identify mechanisms, and we will use the knowledge gained to evaluate a field-ready prototype.

Effects of Ultrasound (US) on TCE Transport



TCE concentration measured as a function of time with and without ultrasonic enhancement. Data for both controls and samples are shown. We applied ultrasound to samples at time = 22 hours. The production of TCE levels above the solubility limit suggests that emulsions may be formed.

Plasma Source Ion Implantation for Advanced Manufacturing

Jay Scheuer

Plasma source ion implantation (PSII) and plasma immersion ion processing (PIIP) can be used to provide economical surface modification to satisfy industrial and DOE stockpile support needs. PSII is a non-line-of-sight ion implantation technique that reduces the complexity and cost of traditional ion implantation. PIIP is a logical extension of PSII that combines ion bombardment with plasma deposition, thus allowing deposition of conformal, adherent coatings with thicknesses of tens of microns. Our project is dedicated to developing and demonstrating PSII/PIIP processes.

We have performed process development and characterization in

support of the industrial implants listed below. A new system dedicated to the development of PIIP processes is now operational. We have performed demonstration implants on actual industrial components and are currently field testing these components. We have conducted implantation experiments at high temperature in collaboration with the Institute of Electrophysics and the Institute of Metal Physics in Ekaterinburg, Russia. A PSII/PIIP process for the deposition of adherent diamondlike carbon films on steels is almost fully developed. We have completed the design and fabrication of a solid-state insulated-gate bipolar transistor (IGBT) modulator that will be

capable of operation at 20 kV with a current capability of 2 kA. This modulator does not suffer from switching storage delay or temperature effects and permits system operation over large temperature extremes.

Publications

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Walter, K.C., M. Nastasi, and C.P. Munson, "Adherent Diamond-like Carbon Coatings on Metals via PSII" (submitted to *Surface Coatings and Technology*).

Walter, K.C., K.T. Kern, J.R. Tesmer, et al., "Nitrogen and Boron Ion Implantation into Electrodeposited Hard Chrome" (submitted to *Surface Coatings and Technology*).

Magnet Design Concepts for the 100-MeV Isotope-Production Facility

E. Wadlinger

If an isotope-production (IP) facility is to be viable at the 100-MeV region of the Los Alamos Neutron Science Center (LANSCE) accelerator, an efficient extraction system is required. The greatest uncertainties are associated with the kicker magnet needed to divert portions of the beam into any new beam line. This magnet must fit into a rigidly defined space within the transition region of the accelerator and must operate in concert with the current accelerator operations systems. In addition, it must in no way degrade beam quality when the

beam is directed to other areas of LANSCE. Because of these constraints, the magnet must be specifically designed and built for this intended application. Project objectives were to evaluate design concepts for the kicker magnet and its power supply and to assess the feasibilities of various design alternatives.

We have developed a conceptual design for a kicker magnet and power supply to be placed in the available space in the transition region to provide a proton beam for a proposed IP facility. Our design study shows the

technical feasibility for delivering the required 100-MeV beam to the IP facility and still delivering the required beam to the proposed long-pulse spallation source (LPSS) facility, the weapons neutron research facility, and the proton storage ring (PSR) at the Manual Lujan Jr. Neutron Scattering Center. LPSS requires proton-beam macropulses of 60 pps and PSR requires 20 to 30 pps of protons, leaving 30 to 40 pps for other users. At the LPSS-proposed 21-mA peak proton-beam current and 1-ms pulses, the IP facility would only need 12 pps to get the required 250- μ A beam. The power supply design is based on a proven and working design for the RIKI (ring-injector kicker) magnet that switches the 800-MeV beam into the PSR.

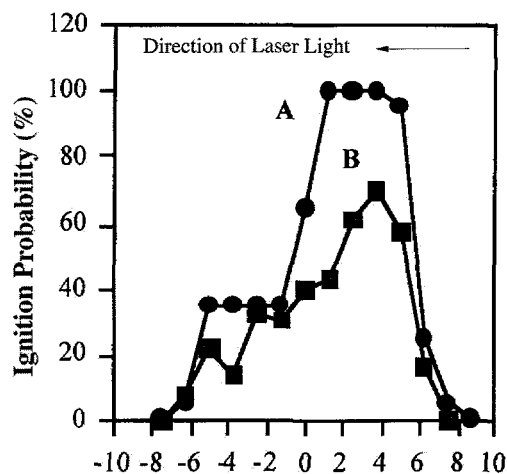
Advanced Ignition of Jet Turbine Engines

James Early

During the past year we have demonstrated several innovative technologies for applying lasers as an alternative to capacitive discharge for the ignition of jet turbine engines. This project focused primarily on two areas essential to the implementation of a practical laser igniter: (1) developing energy-efficient, laser-induced fuel-ignition methods that are effective and reliable, and (2) developing techniques to maintain the transparency of optical surfaces that isolate the laser from the hostile combustion-chamber environment.

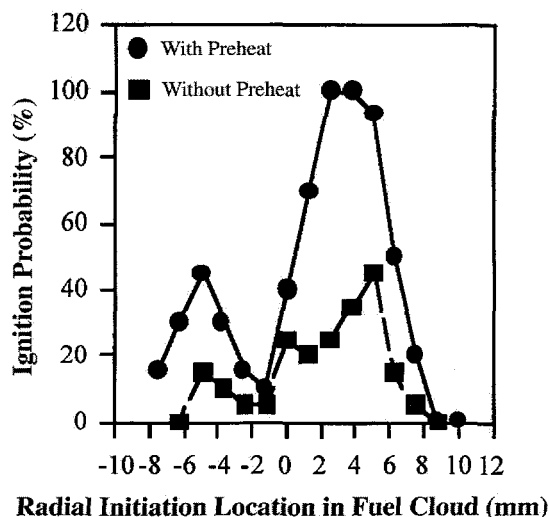
Laser-based ignition concepts employ many laser-wavelength and pulse-format mechanisms to increase both the rate and duration of laser energy delivery. We found that increasing the time the laser light is applied to the fuel medium assists the growth of a stable flame kernel. At the same time, it reduces both laser peak-power requirements and inefficiency in energy utilization.

We used plasma pumping, direct light absorption by fuel components and laser light/material surface interactions as energy-coupling mechanisms. We showed that these innovative ignition methods reliably ignited jet-fuel aerosols over a broad range of fuel/air mixtures and at fuel temperatures as low as -40°F . As shown by the jet-fuel ignition profiles in the accompanying figures, this kind of ignition is superior to conventional laser-spark ignition. We also developed a laser-based method that effectively removes opaque deposits of fuel hydrocarbon combustion residues from laser window surfaces. To date, this R&D effort has resulted in three pending patents, one provisional patent, and one invention disclosure.



Radial Initiation Location in Fuel Cloud (mm)

With the same laser energy (144 mJ), the reliability of jet-fuel ignition is substantially improved by applying the dual laser pulse/plasma pumping method (curve A) over that of conventional laser-spark ignition (curve B).



Radial Initiation Location in Fuel Cloud (mm)

The laser-prevaporization method provides a significant enhancement to jet-fuel-aerosol ignition. Fuel droplets are vaporized by the direct absorption of low-peak-power (30 kW), 3-mm light provided by a free-running Er:YAG laser. The fuel vapor is subsequently ignited by a laser spark produced by a focused, 91-mJ, Q-switched Nd:YAG laser pulse.

Removal of Transuranic Materials from Contaminated Equipment Using Plasma Decontamination

Carter Munson

The primary goal of this project is to develop and demonstrate the utility of plasma-based processes for the removal of transuranic (TRU) contamination from targets of interest to the DOE complex. The first stage of the process has been to design, fabricate, and perform initial tests of a prototype plasma-decontamination system using surrogate materials.

We have designed, fabricated, and integrated a small system ($\sim 0.5 \text{ m}^3$) with a two-stage, cryogenic trapping and recovery system. Examination of the etching characteristics of various gases (CF_4 , NF_3 , SF_6 , etc.) led to the

selection of NF_3 as the plasma precursor gas because of the reduced potential for particulate formation and nonvolatile material deposition. We conducted experiments to examine the removal of various surrogate materials in a number of different target geometries.

We have also conducted a very large scale test ($\sim 3\text{-m}^2$ target area) in another available facility. This test examined the removal of a very hard, chemically resistant, amorphous carbon material from the surface of an extremely complex aluminum target. We used an oxygen plasma in this case as an analogue for the fluorine-based plasma that

would be used to volatilize and remove plutonium or uranium from contaminated surfaces.

Experiments with NF_3 and tungsten (as the TRU surrogate) have demonstrated material-removal rates in a mild, reactive-ion-etching (RIE) mode. These rates are nearly an order of magnitude faster than the material-removal rates we observed in the plasma-immersion mode. We expect significant additional increases in removal rates when the system operates in the combined RIE and sputtering mode.

Publications

Munson, C., E.P. Chamberlin, et al., "Development of Plasma-Based Decontamination of Large Metallic Objects" (23rd International Conference on Plasma Science, Boston, Mass., June 3-5, 1996).

Supporting Technologies for a Long-Pulse Spallation Source

Joey Donahue

We are investigating the accelerator modifications, target-moderator-reflector concepts, neutron-scattering instrumentation, and facility modifications necessary to design a long-pulse spallation source (LPSS) at Los Alamos. We are building on last year's efforts and incorporating technologies and ideas from synergistic activities at the Los Alamos Neutron Science Center (LANSCE), such as the Accelerator Production of Tritium Project, the LANSCE Reliability Improvement Project, and Accelerator-Driven Transmutation Technologies. Major emphasis is on evaluating concepts from an engineering perspective to establish a basis for assessing the technical as well as cost and schedule risks for the proposed LPSS facility.

Our initial work was directed toward modeling the physics of target system and neutron-scattering instrument performance, which was needed to establish the scientific case for the LPSS. We also investigated the accelerator modifications necessary to achieve the 21-mA peak current required for a 1-MW LPSS. We had a successful 32-h accelerator development run at 800 kW of beam power with the LPSS beam structure. This run demonstrated that the LANSCE linac can already deliver 80% of the power needed for a 1-MW LPSS. These efforts supported the LPSS proposal, its preliminary cost and schedule estimates, and a preliminary engineering layout for the target station.

Several external review committees have examined the technical progress of our activities. Based on feedback from the committees, we began to address some of the supporting engineering issues of the target-moderator-reflector system and target station in the latter half of the fiscal year. These include target thermohydraulics and the choppers that are used to shape the neutron pulses. The results of this work have been documented in publications, conference proceedings, and internal Laboratory reports.

Publications

Fitzsimmons, M.R., "Reflectometry at Continuous Wave and Pulsed-Neutron Sources" (to be published in *Nucl. Instrum. Methods*).

Fitzsimmons, M.R., and R. Pynn, "The Performance of Reflectometers at Continuous Wave and Pulsed-Neutron Sources," *ICANS-XIII: Proc. 13th Meeting Int. Collaboration on Advanced Neutron Sources* (1995).

Olah, G.A., P.A. Seeger, and R.P. Hjelm, "Small-Angle Scattering Instruments on a 1 MW Long Pulse Spallation Source," *ICANS-XIII: Proc. 13th Meeting Int. Collaboration on Advanced Neutron Sources* (1995).

Pitcher, E.J., G.J. Russell, et al., "Performance of Long-Pulse Source Reference Target-Moderator-Reflector Configuration," *ICANS-XIII: Proc. 13th Meeting Int. Collaboration on Advanced Neutron Sources*, 323–329 (1995).

Pynn, R., and L.L. Daemen, "The Performance of Neutron Spectrometers at a Long-Pulse Spallation Source," *ICANS-XIII: Proc. 13th Meeting Int. Collaboration on Advanced Neutron Sources* (1995).

Pynn, R., and D. Weinacht, "A Proposal for a Long-Pulse Spallation Source at Los Alamos National Laboratory," *ICANS-XIII: Proc. 13th Meeting Int. Collaboration on Advanced Neutron Sources* (1995).

Russell, G.J., E.J. Pitcher, and P.D. Ferguson, "Coupled Moderator Neutronics," *ICANS-XIII: Proc. 13th Meeting Int. Collaboration on Advanced Neutron Sources*, 495–509 (1995).

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Advanced Oxidation Technologies for Chemical Demilitarization

Louis A. Rosocha

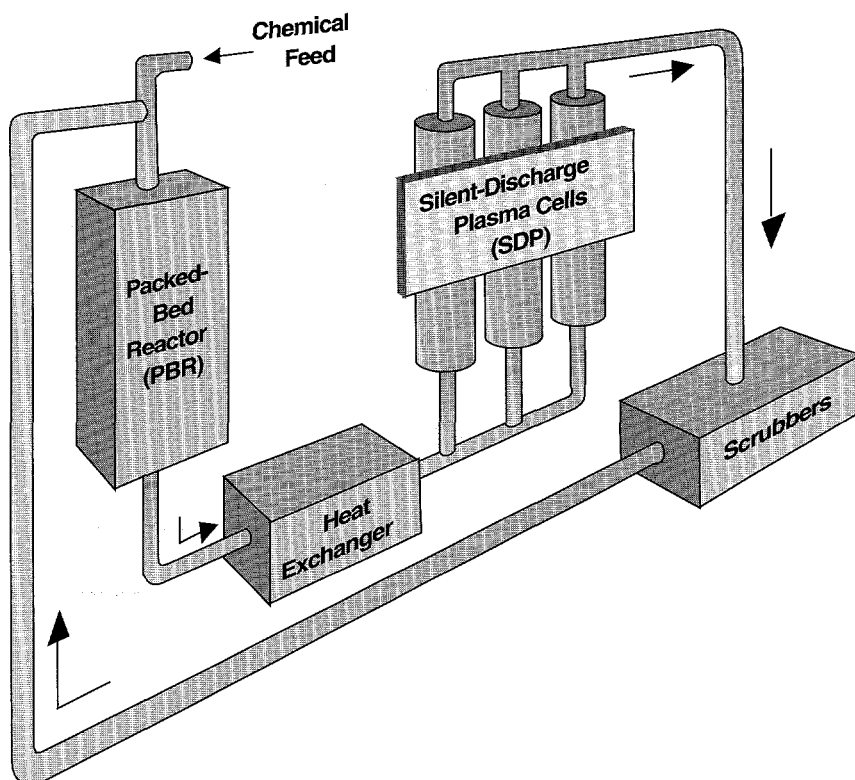
Safely demilitarizing chemical-warfare (CW) agents is a high-priority problem for the Department of Defense (DoD). Historically, the DoD has preferred to destroy CW agents by incinerating them. However, because incineration has many drawbacks (such as leaks, hazardous air emissions, and large secondary-waste streams), the DoD is currently looking for alternative methods that are highly efficient at destroying these extremely toxic chemicals.

Our main objective was to establish an innovative, advanced oxidation

system as a viable process for destroying CW agents, thereby providing a basis for future program development. We focused on testing a system concept in which we first volatilize (and/or oxidize or pyrolyze) a surrogate liquid CW agent using a thermal packed-bed reactor (PBR) and then further process the PBR off-gas with a second-stage nonthermal plasma (NTP) reactor (see schematic diagram). We designed this two-stage system for closed-loop operation to achieve extremely high degrees of agent destruction and to collect and/or control all by-products from the process.

In preparing the apparatus and experiments, we established a projected mass balance for the two-stage unit (based on previous data related to phosphate esters) and compared this projection to incinerator-based processing. We evaluated various CW surrogates and chose the pesticide malathion as our primary simulant. We then designed and constructed a lab-scale PBR/NTP reactor, consisting of a liquid-injection system, an injection-rate meter, an electric furnace, condensers, chemical traps, plasma reactors, power supplies, and chemical diagnostics. In addition, we carried out combined PBR/NTP processing experiments and completed preliminary chemical-processing calculations on carbon dioxide traps, reaction chemistry, by-product distributions, and phase equilibria.

Schematic diagram of an advanced oxidation system for chemical demilitarization with a PBR and an NTP reactor that is based on silent-discharge plasma (SDP). Our system atomizes liquid CW-agent surrogates and then injects them into the PBR, where they are oxidized or pyrolyzed. The PBR off-gas is then fed to the SDP cells (the NTP stage) for further processing. Because we can operate the system in closed-loop mode, we can achieve an extremely high degree of destruction and can capture the by-products of the process. A particularly attractive feature of the system is its ability to operate with oxygen-free feed gases.



Advanced Nuclear Fuel Processing

Larry Avens

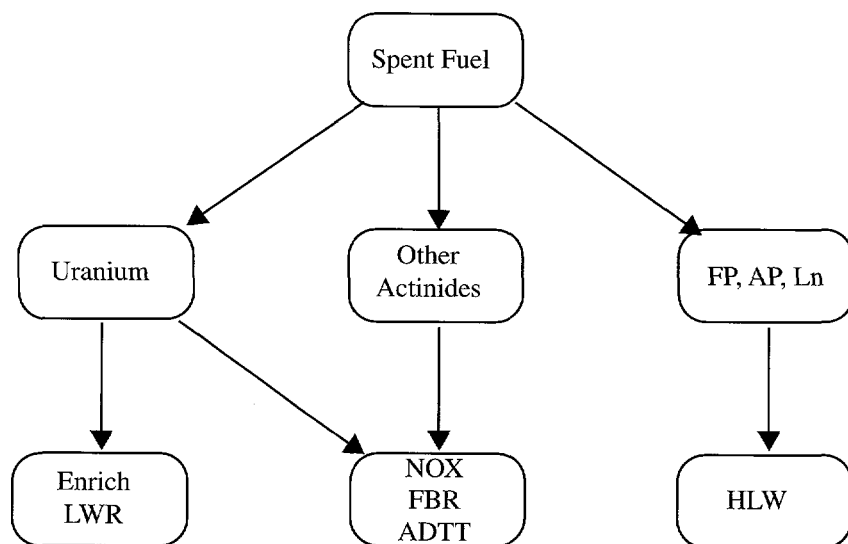
The goal of the project is to determine unique approaches where Los Alamos' expertise in separations and nuclear materials operations can be applied to spent fuel reprocessing. The first figure shows an overview of the technical goals of this proposal. We intend to develop alternative processing technologies and concepts necessary to understand critical elements such as separation efficiencies, material and equipment requirements, and waste generation.

This year we reviewed several separation technologies. These were

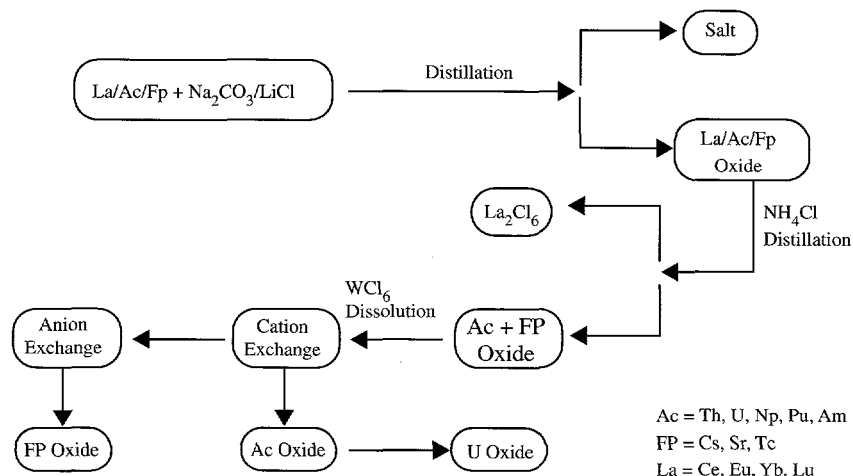
(1) distillation-based separations; (2) pyrochemical separations in metal alloy systems; (3) metal solvent systems for actinide/lanthanide separations; (4) salt-environment methods such as halide slagging; and (5) use of ceramic materials that are constructed to selectively transport or capture elements. Our approach uses chloride salt distillation and recycle methods for plutonium electrorefining salts. Using selective transformations like oxidation and distillation, we have designed a process that separates cesium and strontium from the

actinides, performs a lanthanide/actinide separation, and recovers uranium from the other actinides as illustrated in the second figure.

Initial experiments have shown that significant quantities of actinides, lanthanides, and fission products can be dissolved in a LiCl/KCl eutectic mixture when heated. More importantly, the chloride salts of many of these metals can be converted to their respective oxides by addition of sodium carbonate. We are also investigating the selective halogenation of the lanthanides over the actinides. We have begun investigating tungsten hexachloride and other chloride melts to determine their ability to maintain the desired complex in a low-melting medium.



Destiny of the actinides, fission products, and activation products from spent fuel processing.



Proposed chloride-based, molten-salt separation scheme.

Chemical-Biological Treatment of Heterogeneous Wastes

James Brainard

Heterogeneous wastes (HW)—defined here as wastes containing bulk solids contaminated with one or more components subject to Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Toxic Substances Control Act (TOSCA) or radiation restrictions—are difficult to treat by any single conventional or developing technology. Included in HW are decontamination and decommissioning (D&D) wastes (for example, soil, clean-up debris, and paint-stripper waste); petroleum wastes (hydrocarbons and contaminated soils, metals, and sludges); waste-treatment sludges and combustibles; and filter materials (paper, cloth, wood, solvents, and metals).

Conventional chemical and physical oxidation technologies are not effective in treating these wastes because of problems with one or more of the following: permitting, cost, public perception, and performance.

Using integrated business and technical development activities, we are working to develop, demonstrate, and implement chemical-biological technologies for the treatment of hazardous HW. During the past year we obtained permits and treated actual plutonium-containing D&D waste obtained from storage at Technical Area (TA)-54. We also obtained mass-transfer kinetics equilibrium data and biodegradation kinetics data for the destruction of organic paint-stripper solvents in the modified gas-loop bioreactor that is part of our treatment

system. We applied these data to build and validate a numerical model to simulate the coupled physical and biochemical processes in the bioreactor. In addition, we demonstrated the applicability of HW treatment strategies to the recycle/reuse of Environstrip™ paint-stripper blast media.

Publications

Twary, L.V., R.K. Grumbine, T.M. Foreman, et al., "Integrated Chemical/Biological Treatment of Paint Stripper Mixed Waste," *Proc. of the Third Biennial Mixed Waste Symposium* (Cognizant Communication Corporation, Elmsford, N.Y., 1995), p. 1171.

Twary, L.V., K. Steenhoudt, B. Travis, et al., "Biodegradation of Paint Stripper Solvents in a Modified Gas Loop Bioreactor" (to be published in *Biotechnol. Bioeng.*).

Radionuclide Separations Using Pillared Layered Materials

Norman Schroeder

The objectives of this project are to develop pillared layered materials (PLMs) that can efficiently sorb radionuclides, such as strontium-90, from liquid nuclear wastes stored in underground tanks at DOE facilities and from mixed wastes stored at Los Alamos; to characterize the most promising of these PLMs and test them on actual wastes; and to investigate their sorption mechanisms.

PLMs are layered, inorganic ion exchangers propped apart by metal oxide pillars. This year, we prepared large batches of chromium-, titanium-, and silicon-pillared tantalum tungstate (TaWO_6) materials. To characterize these materials, we used

titrations, surface area measurements, pore size distributions, and capacity measurements. The active sites in these materials were probed with electron paramagnetic resonance, europium fluorescence, and infrared measurements conducted before and after the sorption of gases.

A general conclusion obtained from our data is that there are at least two active sites responsible for cation exchange in these materials. A tentative interpretation of how these active sites function is that one is active at low pH and operates purely by an ion exchange process; the other site is active at high pH, operates by a sorption mechanism, and gives these materials

their strong affinity for strontium. The distribution coefficients (K_d values) for Ca^{2+} , Sr^{2+} , and Ba^{2+} onto the pillared TaWO_6 compounds were determined as a function of ionic strength, pH, surface area, and ionic radius.

The data we obtained show a strong pH dependence and K_d values for the three cations increasing to $>10^4$ above pH 12. Although PLMs removed $>99.999\%$ of the strontium from nuclear waste simulants, their sorption of strontium from actual waste was disappointing. Our analysis indicates that complexants in the actual waste compete effectively against PLMs for the strontium. Destruction of the complexants would make feasible the application of PLMs to the Hanford waste.

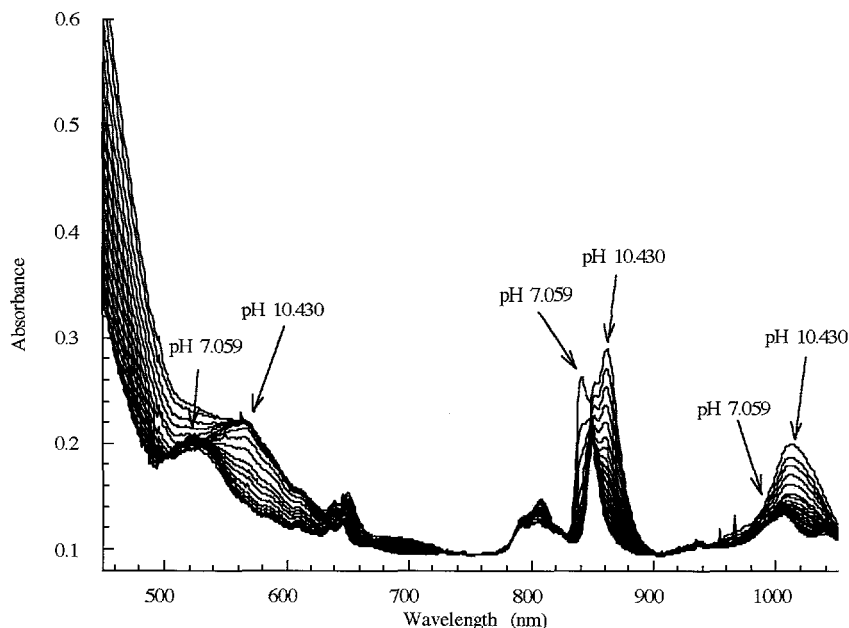
Integration of Advanced, Nuclear Materials Separations Processes

Gordon Jarvinen

We are investigating the fundamental chemistry issues that affect the integration of several promising new separations technologies into nuclear materials synthesis and processing. One of these technologies, hydrothermal oxidation, uses water and an oxidant at high temperature and pressure to efficiently and safely destroy combustible materials. The water stream that results can then be partitioned to give optimal product or waste forms. The successful development of these new technologies will lead to greatly reduced generation of solid wastes from nuclear materials operations.

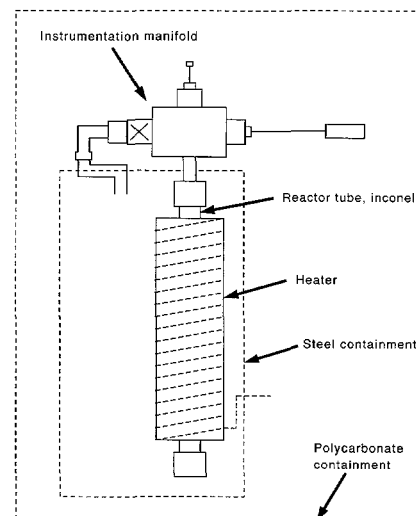
One focus during this year was on the plutonium(VI) carbonate chemistry (including solubility and speciation of plutonium) expected to control the fate of plutonium after hydrother-

mal oxidation of plutonium-containing combustible materials. To measure the solubility of Pu(VI) from oversaturation in carbonate media, we needed a well-characterized, solid-limiting phase. We prepared 500 mg of $^{239}\text{PuO}_2(\text{CO}_3)$ and characterized it by powder x-ray diffraction, extended x-ray absorption spectroscopy, and diffuse reflectance spectroscopy. We initiated solubility experiments using this solid in 0.1- and 5.0-M NaCl solutions under 100% CO_2 . We collected a set of spectrophotometric titration data, some of which are shown in the accompanying plot. A preliminary fit gives formation constants for the tris- and biscarbonate complexes to be $\log b_{130} = 17.7$ and $\log b_{120} = 13.6$, respectively.



A subset of absorption spectra used to determine the formation constants of Pu(VI) carbonate complexes. Experimental conditions were $[\text{PuO}_2^{2+}] = 4.45 \text{ mM}$, $[\text{CO}_3^{2-}] = 12.0 \text{ mM}$, ionic strength = 0.1-M NaClO_4 , temperature = 25°C , and $\text{pH} = 7.059\text{--}10.430$. The spectroscopic peaks clearly shift to higher wavelengths as the pH increases. To determine the formation constants, we fit these peak shifts to a model in which the formation constants and spectra of the individual complexes are free parameters.

A second focus was on implementing a capability for hydrothermal R&D on plutonium-containing materials using small-batch reactors. We designed and built several hydrothermal batch reactors (see accompanying diagram) that we will install in a glove box at the Plutonium Facility. We will conduct plutonium-speciation experiments on 2- to 2.5-mL mixtures of solution and solids at pressures of up to 6000 psi and temperatures of $500^\circ\text{C}\text{--}600^\circ\text{C}$ in these reactors. When we tested these batch reactors on non-radioactive solutions, we found that hydrothermal processing conditions oxidized Ce(III) to Ce(IV) and Cr(III) to Cr(VI), supporting our expectation that plutonium compounds will be oxidized to Pu(VI).



Schematic drawing of a hydrothermal batch reactor that we constructed for this project. We will install it in a plutonium-handling glove box.

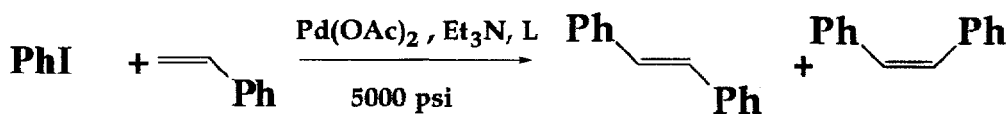
Catalysis for Alternative Feedstocks

William Tumas

In this project we focused on technical and program development work in catalysis and supercritical fluid chemistry to strengthen the Laboratory's capabilities and to position Los Alamos for future programs. The program development activities focused on working closely with industry, DOE, and the EPA to launch new initiatives in catalysis for next year and beyond. We expect the technical work on catalytic processes in supercritical carbon dioxide to yield innovative, environmentally benign

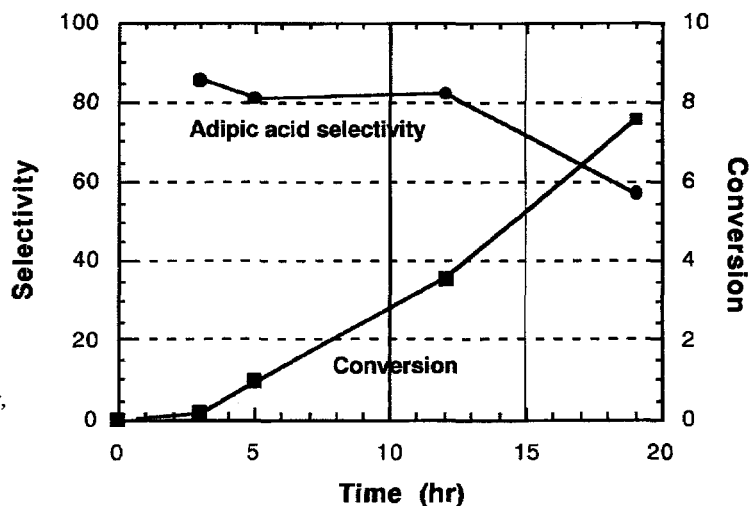
processes utilizing carbon dioxide as a solvent and a potential reagent. This work focused on two classes of reactions that are industrially significant and could lead to extensive waste minimization/solvent replacement: (1) palladium-catalyzed reductive carbon-carbon bond-forming reactions (Heck reaction) to produce pharmaceutical intermediates, as shown in the first figure, and (2) cobalt-catalyzed air oxidations of cyclic hydrocarbons to produce polymer intermediates, as shown in the second figure.

Our work on the Heck reaction revealed supercritical carbon dioxide can be used as an alternative solvent for the Heck reaction. We examined a number of catalysts for the reaction of iodobenzene with styrene in the presence of triethylamine. Perfluorinated phosphine catalysts dramatically increased conversions to 99% after 12 hours at 90°C and 5000 psi. We have found CO₂ to be an effective cosolvent for the direct cobalt-catalyzed air oxidation of cyclohexane and cyclohexanone to adipic acid. Oxidation of cyclohexane at 95°C produced adipic acid with selectivities higher than those of conventional solvents (>80%) at low conversions (up to 4%). Direct air oxidation of cyclohexanone proceeds at higher rates.



L = Ligand	Time	T(°C)	Conversion	trans-Stilbene	cis-Stilbene
none	12 h	90°C	19%	>99%	----
(C ₆ H ₅) ₃ P	4d	90°C	37%	93%	7%
(C ₆ H ₁₁) ₃ P	12 h	90°C	14%	>99%	----
(C ₆ F ₅) ₃ P	12 h	90°C	99%	94%	6%
(C ₆ F ₅) ₃ P	24 h	40°C	51%	94%	6%

Summary of palladium-catalyzed carbon-carbon bond forming (Heck reaction), illustrating higher conversions using fluorinated phosphine ligands.



Oxidation of cyclohexane at 95°C in CO₂/HOAc, illustrating high selectivity for the formation of adipic acid at conversions up to 6%.

Separation Science and Technology: Membrane-Based Separations and Destruction Processes

Barbara F. Smith

This project combines advanced separations and destruction technologies with the objective of adapting them to industrial needs. Specifically, our research focuses on the following areas: synthesizing new extractants for removing valuable or hazardous metal ions from industrial waste and process streams or from groundwaters, producing membranes that will selectively separate industrial gases, and designing membrane or supported systems that will selectively oxidize or destroy hazardous organics.

Our first goal was to prepare water-soluble, chelating polymers that could be used to remove or recover valuable or toxic metals from a variety of process or waste streams. Industry is interested in advanced, metal-ion separations because these technologies lead to lower operating and waste treatment costs. This year, we prepared nine new, water-soluble, metal-binding polymers, and some have shown selectivity for certain oxyanions (such as tungsten, molybdenum, arsenic, and selenium), even in the presence of a high salt concentration (for example, 1-M NaCl).

Another goal was to separate fission products such as cesium and strontium from high-level radioactive wastes or from contaminated groundwaters using a specific extractant, cobalt dicarbollide. As a soft anion, cobalt dicarbollide will selectively bind cesium and strontium and pull them from an aqueous phase into an organic phase. Current processes rely on hazardous solvents such as nitrobenzene; we modified the process to use diethylbenzene, an environmentally benign organic solvent, in place of nitrobenzene. We demonstrated simultaneous cesium and strontium

removal from high-level waste surrogates using this new system.

We were also interested in developing advanced electrochemical reactors that would improve our ability to separate and treat waste. We successfully demonstrated a new electrochemical-cell design in which the cell voltage at a current density of 300 mA/cm² was just 1.7 V; the cell voltage in commercial units is 3.2 V. The resulting systems can provide more-energy-efficient organic destruction than the commercial units can.

Another area we studied was advanced membrane materials for separation of industrial gases such as hydrogen. We installed a polymer-spinning unit that produces hollow fiber membranes, a favored membrane geometry for efficient separations. We used this unit to spin membrane materials, such as polysulfone and polyaniline, into microporous and ultraporous hollow fibers, and we evaluated the spun systems for gas separations. We also compared the separation properties of these fibers with the separation properties of high-strength, highly conductive (>50 S/cm), polyaniline solid fibers. In addition, we demonstrated the feasibility of producing ultraporous and microporous polyetheretherketone flat-sheet membranes.

We are also developing "smart" filters, which will selectively bind and, if designed properly, potentially destroy organic materials. We successfully synthesized a number of host polymers for organic materials, and we demonstrated that these host polymers have the nanoporosity necessary to absorb organic contaminants from water. We measured the equilibrium

constants of the host polymers for a number of systems and successfully fabricated optical-quality membranes from these polymers.

Our final goal was to develop in situ photocatalytic reactors for selective oxidation of organics. These systems may allow a valuable oxidized organic product to be synthesized from an organic waste stream. We are focusing our organic-oxidation studies on phenolic materials in aqueous streams and arenes in the gas phase. Currently, we are collaborating with Bechtel on applying species-selective oxidation technology to its industrial symbiosis goals and on extrapolating the technology to metal removal.

Publications

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Winokur, M.D., J. Maron, and B.R. Mattes, "Processing Induced Changes in the Local Structure of Amorphous Polyaniline Using RDF Analysis," *Macromolecules* **28** (13), 4475 (1995).

Microwave Processing Improvements for Methane Conversion to Ethylene

Ray Stringfield

The objective of this project was to investigate microwave-enhanced catalysis. Published work by others had demonstrated improved selectivity in microwave-driven catalytic conversion of 2-methylpentane to its isomers.

Our accomplishment was reproducing their experiment and discovering that there is no improvement in selectivity using microwaves. The selectivity at a given conversion was the same for both microwave-heated and conventionally heated catalyst beds. Meetings with the authors of the earlier work led to the conjecture that

their catalyst had not been prepared properly, which led to anomalous, low selectivity for their conventional heating runs. Even though we found no improvement in selectivity with microwaves, microwave processing still offers the promise of rapid heating adjustments and low thermal inertia—aids to quality manufacturing.

We developed and characterized an optical temperature diagnostic suitable for use on a microwave applicator in this project. This pyrometer can measure the temperature of small-scale features on the catalyst bed. In addition, it has a fast response that

can follow the rapid heating often encountered in a microwave processing system. We studied the behavior of the microwave applicator system and developed theoretical models that yield insights about the stability and control of the system.

Publications

Nelson, E.M., "Enhancement of Thermal Stability in Microwave Applicators by Mismatching and Detuning," *31st Microwave Power Symp. Proc.* **31**, 108 (1996).

Mathematics and Computational Sciences

Data Resources and Sample Applications for Information Analysis in Chemical and Biological Warfare Defense

Kevin Buescher

The Laboratory has extensive information analysis capabilities. Our goal in this project was to identify representative applications for these in the area of chemical and biological warfare defense. In particular, we focused on developing methods for detecting the outbreak of diseases and for predicting their evolution. In particular, we examined existing mathematical models for the statistical progression

of infected individuals from a dynamical systems viewpoint. We found that we could express a number of disease models in a common form and that we could transform these models in a way that allows us to perform on-line estimates of their model parameters in a computationally efficient manner. Using this technique, we could track diseases in an automated and cost-effective manner.

After reviewing the literature and talking with experts in the field, we have determined that the greatest need in this area is for epidemiological models that account for spatial and transport aspects of disease spread. The Laboratory's simulation capabilities might help to address this need. For example, we could link transportation and climate simulations to a model of infection mechanisms to better predict the evolution of an outbreak.

In addition, the Laboratory's analysis capabilities could prove to be very useful in mining morbidity and disease data to locate similar cases that could indicate the onset of an epidemic or an attack.

Information-Handling/Data-Fusion Technologies to Extract and Analyze Export Information

Harry Forehand

Proliferant nations generally do not have the technical capability and industrial infrastructure to produce nuclear weapons without assistance from nuclear weapons states or advanced-technology countries. Hence they may procure the technology, both material and hardware. We planned to develop an information-handling/data-fusion tool to extract and analyze export information to look for attempts by proliferant countries to

acquire such technology. Export information, both dual-use, export-controlled, and Schedule B (*Statistical Classification of Domestic and Foreign Commodities Exported from the US*) are generally available electronically. This project was intended to investigate automated data-handling and link-analyses tools to develop techniques for rapid evaluation of technology-transfer mechanisms via export information.

We researched commercially available databases containing export commodities information for application to our investigation and had extensive discussions with the Department of Commerce (and other organizations involved in export-controls-data review). Yet it became clear that the data sources we needed did not contain sufficient and necessary information to derive indicators of proliferation. In addition, none of the commercially available data contained sufficient detailed data to do the job adequately, nor was the data likely to be available in the near future. The project was therefore terminated before its normal term.

Intelligent Controllers for Battlefield Simulations

Chris Barrett

In this project we are developing, testing, and demonstrating new methods for producing intelligent computer-generated forces, battlefield simulations in which computer codes decide the behavior of military forces. These battlefield simulations are an area of growing importance and interest to the Department of Defense (DoD). Our new methods are based on two advanced simulation technologies: intelligent control and adaptive systems. In intelligent control technology, we formally emulate the control process of the real system using a rule-based, expert systems approach that improves over time by adding new rules. In adaptive systems technology, the adaptive systems software learns and adapts its tactics from synthetic battlefield experiences generated by the simulation.

The simulation environment we are using is called JointSim; the Air Force, Army, and DoD have been developing this environment over the past few years, and it serves as an excellent test bed and proving ground to introduce the Laboratory's research advances in battlefield simulations to the DoD. In FY96 we developed a command and control architecture that the joint U.S./U.K. working group on command and control standardization accepted as their standard reference model. We also developed a genetic algorithm that learns new tactics for systems not yet in the DoD force structure.

Publications

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Nagel, K., C. Barrett, and M. Rickert, "Parallel Traffic Microsimulation of Traffic by Cellular Automata and Application" (submitted to *Transportation Res. C*).

Rasmussen, S., C. Barrett, and M. Olesen, "Dynamical Hierarchies: A Summary" (First International Conference on Artificial Life and Robotics, Oita, Japan, February 2-10, 1996).

Reidys, C., "Mappings in Random Structures" (submitted to *SIAM J. Discrete Math.*).

Stroud, P., "An Adaptive Airborne Laser Flight Controller" (submitted to *IEEE Trans. Systems, Man, and Cybernetics*).

Stroud, P., "Simulation-Based Learning in Knowledge-Based Controllers" (1996 International Symposium on Intelligent Control, Dearborn, Mich., September 1996).

Visualization Capability for Nonproliferation and Emergency Training: A "Poor Man's" Virtual-Reality System

George Papcun

We have developed means to take an ordinary photograph or video image and rapidly transform it into a three-dimensional virtual-reality environment of what is shown in the image. This capability can be applied to nuclear nonproliferation, to emergency management, and to related situations. For example, if a photograph can be obtained of some location that has dangerous chemicals stored in it, a virtual-reality environment would let workers carry out practice runs for dealing with the chemicals without exposure to the dangers of the actual environment. To take another example, let us suppose that a limited number of photographs are available of clandestine locations where nuclear materials may be stored or manufactured. In such situations, a virtual-reality representation would allow inspectors to make measurements, determine what additional information is needed, and so on.

Our system provides the operator with a set of computer programs that he or she can use to transform the image into its three-dimensional representation. Included in the system is a tutorial that teaches the operator how to use the system. Because our system runs on an ordinary personal computer, it is relatively inexpensive and portable.

In the course of our research, we have developed new means to make measurements of complex shapes, such as faces. This aspect of our work can be applied to recognizing images of people.

Modeling for Environmentally Conscious Manufacturing

Richard LeSar

This project focused on creating an integrated approach for developing simulation tools for environmentally benign manufacturing. We developed casting simulations that would yield an accurate prediction of materials' microstructures and properties, which, in turn, would enable development of near-net-shape casting methods with little waste. The specific objectives of this project were to develop methodology to couple microscopically based solidification models to fluid flow and to implement these techniques within existing computational fluid dynamics codes. Progress this year was made in the following three areas.

Modeling of Equiaxed Eutectic Solidification. We developed a model of equiaxed eutectic solidification that couples the microstructural level (nucleation, growth, and impingement of the grains) with the macroscopic level of heat flow. The principal outputs of the model are temperature and solid fraction fields and detailed pic-

tures of the microstructure, which enable us to analyze any microstructural parameters of interest as a function of cooling rate and other processing conditions.

Modeling of Quiescent Crystallization of Semicrystalline Polymers. We developed a multiscale model for the crystallization of polymers that accounts for heat diffusion at the macroscopic scale; grain nucleation, growth, and impingement at the mesoscopic scale; and fibrils growth at the microscopic scale.

Direct Modeling of Dendritic Growth. We developed a model that reproduces the growth of solutal dendrites, i.e., the destabilization of a spherical nucleus into a dendritic grain with primary, secondary, and tertiary dendrite arms.

We are planning to implement these successful microstructural models within a new casting code being developed under the Accelerated Strategic Computing Initiative.

Publications

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Charbon Ch., and S. Swaminarayan, "A Multiscale Model of Polymer Crystallization II: Crystallization of a Macroscopic Part" (submitted to *Polymer Engin. Sci.*).

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Low-Speed Flow Hydrodynamics

John H. Cerutti

This project has led to the development and application of a new tool, called Telluride, for the simulation of casting processes. Our efforts have allowed Telluride to model key processes present in Los Alamos foundries.

We formulated and implemented a second-order-accurate algorithm for the robust solution of the incompressible Euler equations. We incorporated a Runge-Kutta time-integration scheme (ideally suited for unstructured meshes) into our volume-tracking algorithm. We also devised and tested in two dimensions a new "full remap" time-integration scheme. The volume-tracking and fluid-flow algorithms give Telluride a

unique interfacial flow capability, as demonstrated by our simulations of a drop splash and the filling of a box. In addition, we implemented an interfacial-surface-tension model (essential for mold-filling scenarios) and devised and implemented a novel back-diffusion model for alloy solidification. Efficient (>90%) parallelization of our algorithms was demonstrated on several multiprocessor platforms.

We performed isothermal "mold-filling" simulations (neglecting heat transfer) with conditions representative of our foundries (e.g., a top fill of a box mold). We are presently simulating the fill of a copper chalice cast in our

foundries. We also performed heat transfer/solidification simulations of a gravity-poured, cast-uranium cylindrical shell; we were successful in reproducing experimental solidification times.

Because of our successes in this third (and final) year of the project, the Accelerated Strategic Computing Initiative Program has provided funding for further Telluride development.

Publications

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Rider, W.J., and D.B. Kothe, "Volume Tracking Reconstructed" (submitted to *J. Comput. Phys.*).

A New Model to Estimate Regional Emissions Inventories

Michael Williams and Michael Brown

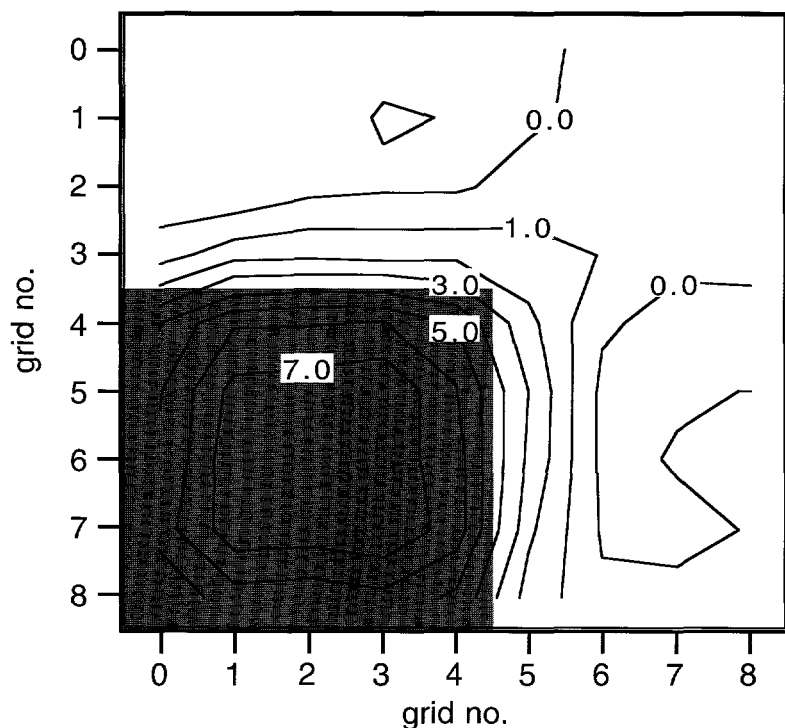
With collaborators from the University of Southern California (USC), we are optimizing a new model for computing gridded air-pollution emissions by integrating meteorological, photochemical, and hybrid receptor models. At present, estimating gridded emissions inventories is seen as the weakest link in air-quality evaluations. Our model, called SITEOF for Source Identification through Empirical Orthogonal Functions, uses existing ambient concentration measurements of pollutants and then runs "backwards" to derive the pollutants' source location and strength. By applying a statistical empirical-orthogonal-eigenfunction approach, SITEOF produces emissions inventories over

an entire city on 1-km² grids (see first figure).

Since emissions inventories are not known with any certainty in the real world, we have tested our new model with synthetic concentration fields (see second figure). These fields are produced by a Laboratory-developed air-quality modeling system—the higher-order turbulence model for atmospheric circulation (HOTMAC) and the random particle transport and dispersion (RAPTAD) model—with user-specified emissions inventories. Using 30 days of model-computed synthetic hourly concentration fields, we are investigating the most effective ways to construct gridded emissions from the assumed inventories. With

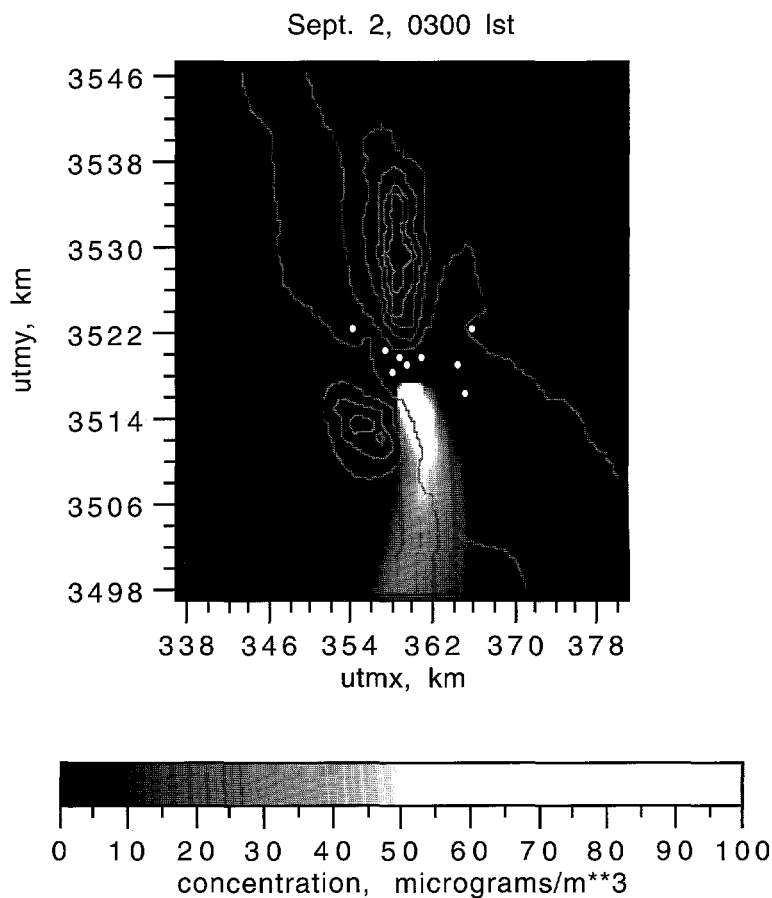
our USC collaborators, we are also determining the optimum location and number of measurement sites needed to calculate an emissions inventory.

As a prelude to the next step in developing our SITEOF model, we coordinated an extensive volatile organic compounds (VOCs) canister study as part of a larger field experiment in the El Paso/Ciudad Juarez region. The field experiment was a joint effort with the Texas Natural Resource Conservation Commission and the US Environmental Protection Agency. Measurements show significant correlation between carbon monoxide and both acetylene and *trans*-2-butene (see third figure), indicating that routinely measured CO might be used as a surrogate for other VOCs and thus be used as an input parameter to the SITEOF model when studying reactive species.

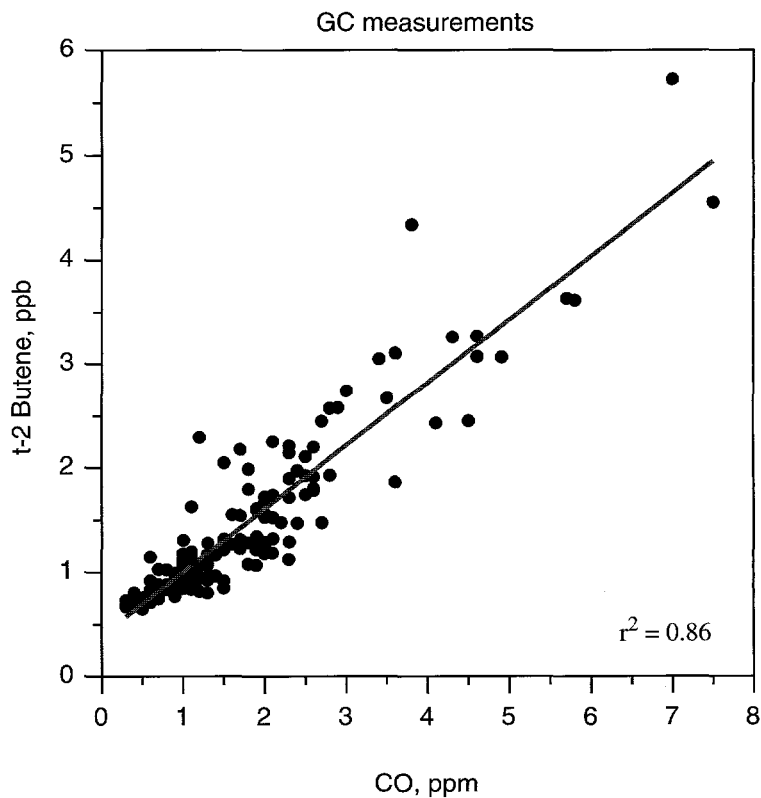


Example of gridded emissions fields generated with SITEOF from synthetic concentration fields produced by a simple Gaussian dispersion model. The gray box represents an emissions source of 8 units strength; the contours depict the computed emissions inventory. Agreement is good for this simple case; we are using HOTMAC and RAPTAD data to optimize the SITEOF model for more realistic (complicated) scenarios.

A one-hour average concentration field computed with the HOTMAC/RAPTAD modeling system for a 1-km² area source of a nonreactive pollutant (CO) in the El Paso/Ciudad Juarez region. Near the source, the plume travels close to the ground and is transported to the south-southeast by low-level winds; as the plume mixes upwards, it bends to the south-southwest and is carried along by upper-level winds. Thirty days of hourly synthetic concentration, wind, and boundary-layer-depth fields were produced and fed into the SITEOF statistical model. The computed emissions inventory was then compared with the known emissions inventory that was input into HOTMAC/RAPTAD. The white dots in the figure are monitoring stations.



Gas chromatograph measurements of carbon monoxide (a nonreactive air pollutant) and trans-2-butene (a highly reactive ozone precursor) taken in El Paso during an extensive field experiment this past summer. The high correlation between the two sets of measurements indicates that the routinely measured CO can be used as a surrogate for VOCs like trans-2-butene, which are seldom measured for thirty consecutive days at multiple locations. From the data collected, we will determine statistical relationships between CO and relevant VOCs.



Improving Industrial Performance through Integrated Process Simulation, Control, and Optimization: Modeling Atoms to Enterprise

Anne D. Henriksen

The goals of this project were as follows: (1) develop an integrated, object-oriented system model of the top three layers of the atoms-to-enterprise hierarchy; (2) develop process models of selected steel-production unit operations and molecular-level models of selected steel-making processes for eventual integration into the model of the top three layers; (3) establish relationships with members of the steel industry; and (4) generate external funding from either DOE or cooperative research and development agreements (CRADAs) for follow-on work.

We have divided the accomplishments of this project into two categories: technical and program develop-

ment. Technical accomplishments include the following. We developed an object-oriented system simulation of selected processes on the top two levels of the atoms-to-enterprise hierarchy and integrated them with all the elements on the third (i.e., manufacturing) level. We developed several models, including a blast-furnace, mass-balance process model (at the unit-operations level) for integration with the system simulation; a basic oxygen-process (BOP), carbon-end-point model (at the unit-operations level) based on nonlinear-model, predictive control; and a BOP kinetics model (at the molecular level) for predicting carbon endpoint, which we will integrate with the nonlinear, predictive-control model.

Under program development accomplishments, we visited three steel companies (Inland, DOFASCO, and Bethlehem) and established a working relationship with DOFASCO. We also established a relationship with the Association of Iron and Steel Engineers (AISE), the steel industry professional organization, with the following outcomes: we (1) obtained a prioritized list of three proposals that AISE was willing to fund for joint work with Los Alamos; (2) hosted a meeting of over 30 AISE members at Los Alamos to present the Laboratory's metals- and modeling-related work; and (3) obtained funding from DOE for a follow-on project on blast-furnace stove control.

Publication

Henriksen, A.D., "A Framework for Hierarchical Object-Oriented Simulation Modeling of a Steel Manufacturing Enterprise," in *The 1996 Object-Oriented Simulation Conf. Proc.*, C. Roberts and J. Wallace, Eds. (Society for Computer Simulation, San Diego, Calif., 1996), pp. 123-131.

National Environmental/Economic Infrastructure System Model

Robert Drake

We are working to develop a new methodology for the macroeconomic modeling of national environmental and economic problems. We are doing this because the current suite of the nation's best macroeconomic forecasting models is well known for its failure to produce accurate analyses. In the past, the computational complications of simultaneously linking all of the nation's economic activities have prevented researchers from designing adequate policy analysis tools. This year we have explored, studied, and synthesized the current literature concerning the microbehavioral foundations of macroeconomic analysis; we focused especially on the linkages of natural resource markets and environmental policy to the national economy.

We have produced a new approach for the macroeconomic modeling of national environmental and economic problems. The concept is based on the integration of microsimulation methodologies with the new microfoundations of macroeconomic theory. This year we completed the background analytical research, and we briefed Laboratory program and division office leaders on our project goals and technical prospects. We have generated significant internal technical support and program interest, and we have established external contacts with the U.S. intelligence community and the Department of State. We investigated a related project that uses massively parallel processing at Sandia National Laboratories, and we negotiated with them concerning

possible coordination of our organizations' efforts.

We investigated the development of an environmental technology evaluation tool that uses simulation science techniques. We experimented at making such a tool, trying out various ideas from other similar projects, such as our Transportation Analysis and Simulation System (TRANSIMS) models. We demonstrated that the prospects for applying simulation techniques to macroeconomic modeling are viable. DOE Environmental Management policymakers as well as Laboratory environmental decision-makers have expressed interest in further development and use of the tool. They are interested in immediately applying it to determine the most cost-effective method of paying for the DOE complex cleanup within a competitive market framework. We have already developed a very simplified model to simulate the Laboratory's transuranic solid-waste stream.

Global Nuclear Material Flow Model

Jared S. Dreicer

The goals of this project are to

- (1) characterize the global inventory of nuclear weapons material (plutonium and highly enriched uranium),
- (2) characterize the safeguards accounting and management and control methodologies and enumerate the associated resource requirements,
- (3) develop macro-system analytical capabilities to estimate future quantities of nuclear material, estimate the impact on material inventory of disposition options, and estimate future resource requirements for nuclear material management and control,
- (4) develop a visual representation of the information related to nuclear facilities and sites and the nuclear material flow among and within countries, and support the development of other pertinent algorithmic capabilities necessary to undertake further global nuclear material-related studies.

Our results include the following: A prototype analytical model has been developed to enable systems analysis of a variety of global, nuclear material management issues. The model can

assess future quantities and disposition of nuclear material, estimate future resource requirements for nuclear material management and control, address material-transfer issues, and examine nuclear fuel-cycle, facility-specific issues. We can represent visually the global disposition of plutonium and highly enriched uranium as well as facility-specific data.

We have completed two nuclear-proliferation studies. The first study indicated potential areas that require strengthening in the International Atomic Energy Agency's *Safeguards Criteria*. We specifically showed that there could be proliferation activity that might go undetected under the current safeguards criteria. In the second study we estimated the amount of plutonium likely to have been produced in a North Korean research reactor during the entire period it operated.

Publications

Dreicer, J.S., and D.A. Rutherford, "Fissile Material Disposition and Proliferation Risk" (International Spent Nuclear Fuel and Fissile Material Management, Reno, Nev., June 16–20, 1996).

Dreicer, J.S., and D.A. Rutherford, "Fissile Material Proliferation Risk," *Nucl. Mater. Mgmt.* **XXV** (1), 30 (1996).

Dreicer, J.S., and D.A. Rutherford, "Global Estimation of Unreported Plutonium Production in Thermal Research Reactors," *Nucl. Mater. Mgmt. Proc.* **XXX**, 1050 (1996).

Dreicer, J.S., and D.A. Rutherford, "Global Nuclear Material Control Model" (International Spent Nuclear Fuel and Fissile Material Management, Reno, Nev., June 16–20, 1996).

Atomic and Molecular Physics

Measurement Criteria Analysis for Krypton, Xenon, and Hydrogen (Hydrogen/Deuterium/Tritium) Isotopes and Concentration Variability at Distance

Bryan Fearey

Our goal is to assess the feasibility of and technology for remotely sensing noble-gas fission products emitted from reactors in order to determine the reactors' operating parameters and history. The importance of measuring xenon and krypton isotopic ratios has increased substantially as concerns about global nuclear proliferation have grown in recent years.

We have modeled and performed a systems analysis for the production and atmospheric dilution of noble-gas fission isotopic ratios, addressing such issues as the relative isotopic variation as a function of nuclear fuel composition and reactor history and type. Of particular importance in our analysis was the question of how to back-calculate process parameters given

noble-gas isotopic data. We also analyzed the effect of measurement uncertainties on the estimated parameters. The results of our work indicate that noble-gas monitoring should be experimentally feasible.

Publications

Nakhleh, C.W., W.D. Stanbro, L.N. Hand, et al., "Noble-Gas Atmospheric Monitoring for International Safeguards at Reprocessing Facilities" (to be published in *Science and Global Security*).

Geoscience, Space Science, and Astrophysics

The Carpinteria Reservoir Redevelopment Project

Richard P. Kendall

The central goal of this project was the development of a Web-based, reservoir-management system that would allow multi-user access to large volumes of complex data and remote access to common user software tools. The objective was to greatly enhance the quality of analysis that could be done on complex systems such as an oil field by a small team of professionals like those found in a typical independent oil- and gas-producing company (there are about 8000 such companies in the United States).

We successfully developed a client-server system that can support the use of best-of-class petrotechnical software. A distributed-object data store formed the "backplane" of this system. This data store (a data model and a collection database) complies with industry standards (Petrotechnical Open Software Corporation), can be queried from remote sites via the Web, and can be maintained by the "owners" of the data at remote sites.

We tested the reservoir management system and actually used it to evaluate new field-development plans for the Carpinteria offshore field. Carpinteria was chosen as the location for first application of the management system because the field has experienced a production decline of more than 10 years duration—typical of some 20 offshore California fields. The management system we designed supports professionals (geoscientists and engineers) at five separate locations (Long Beach, Carpinteria, Ventura, Houston, and Los Alamos). In effect, the system enabled these professionals to form a "virtual enterprise" for the reservoir-management study, and they have used the tools and approaches developed in the project to formulate and evaluate alternative oil recovery strategies for the Carpinteria field. This project is a good example of the use of the rapidly evolving National Information Infrastructure to support a technical project.

Publications

Kendall, R.P., M.B. Lee, A.G. Sgro, et al., "Tools for the Oil & Gas Virtual Enterprise" (SPE 72nd Annual Technical Conference and Exhibition, San Antonio, Tex., October 5–8, 1997).

Kendall, R.P., E. M. Whitney, R. Paul, et al., "A Simulation-Based Reservoir Management Program" (SPE 72nd Annual Technical Conference and Exhibition, San Antonio, Tex., October 5–8, 1997).

Kendall, R.P., E. M. Whitney, R. Webster, et al., "Advanced Reservoir Management for Independent Oil & Gas Producers" (SPE 72nd Annual Technical Conference and Exhibition, San Antonio, Tex., October 5–8, 1997).

Kendall, R.P., E. M. Whitney, R. Webster, et al., "Improved Oil Recovery for Independent Oil & Gas Producers" (SPE 72nd Annual Technical Conference and Exhibition, San Antonio, Tex., October 5–8, 1997).

Sgro, A.G., R.P. Kendall, J.M. Kindel, et al., "Improved Oil Recovery for Independent Oil and Gas Producers" (SPE Improved Oil Recovery Symposium, Tulsa, Okla., April 21, 1996).

Voskanian, M.M., R.P. Kendall, E.M. Whitney, et al., "A Simulation-Based Reservoir Management Program" (SPE Western Regional Meeting, Anchorage, Alaska, May 22–24, 1996).

Satellite-Based Laser Windsounder

John Schultz

Our objective for this project is to assess the technical feasibility of using satellite-based laser wind measurement systems to improve proliferation detection capabilities. At present, much of the United States' ability to detect proliferation depends on physically sampling wind-borne effluents from suspected facilities, but the effectiveness of this technique is severely limited by inadequate knowledge of wind patterns. From our interactions with the relevant operational proliferation detection organization, we confirmed that better wind measurements would contribute greatly to long-range and regional proliferation detection. We also obtained enthusiastic programmatic support and useful assessments of measurement requirements and priorities from the operational users.

We evaluated four potential laser wind-sensing techniques and selected the incoherent Doppler technique. It

uses an interferometer to measure the Doppler shift in near-ultraviolet laser light scattered from aerosols and particulates entrained in the atmosphere. Our choice was based on the simplicity and maturity of the required lasers and interferometers and on the potential for using the same system to measure other atmospheric parameters of interest, such as water vapor content, temperatures, and various cloud properties.

We completed a conceptual design study to identify the technical challenges inherent in a relatively inexpensive, low-risk, proof-of-concept small-satellite mission appropriate to Los Alamos' technical capabilities. The major challenges that we identified were the system's weight, power consumption, laser scanning pattern and pointing knowledge, and techniques for assimilating measured data into atmospheric transport models. Our conceptual design was based on the Fabry-Perot interferometer tech-

nology that has been used for all known incoherent Doppler lidar systems to date. During the course of the study, however, it became apparent that much simpler optical systems based on Mach-Zehnder interferometers promise equivalent performance with substantially reduced weight and power consumption. At the conclusion of the study, we built a breadboard Mach-Zehnder interferometer-based system and used it to qualitatively verify these predictions. To quantitatively verify the benefits of systems based on Mach-Zehnder interferometers, we have developed detailed plans that include constructing and testing a fieldable ground-based wind measurement system in collaboration with the University of Wisconsin and performing numerical data assimilation studies.

Publications

Czuchlewski, S.J., M.J. Brown, G.H. Nickel, et al., "Preliminary Analysis of Lidar Techniques for Regional Meteorological Studies," *Proceedings of the Gas Lasers Conference, SPIE 2702*, 52-64 (1996).

Conditioning Geological Reservoir Realizations with Time-Dependent Data

Richard P. Kendall

The goal of this project was to provide a preliminary geostatistical characterization of the Carpinteria offshore field in order to support the future stochastic simulation of its geological attributes. This oil reservoir is typical of some twenty offshore fields near the California coastline. Most of these fields are experiencing a serious decline in oil production, which we

can hope to stem only with the application of the most advanced recovery techniques. One such technique is geostatistics to reduce the inherent uncertainty in the geological description of the field.

The most important finding of this work was the identification of potential "pay" layers of the field, based on the underlying statistics of the field

measurements (primarily well logs). These layers have the highest oil storage capacity and conductivity. The study also suggests that reservoir attributes correlate over distances of at least 500 ft. Since the median distance from a well to its nearest neighbor is about 250 ft, this means that improvements in modeling can be expected if stochastic simulation methods are used.

Improved Atmospheric Transport for Risk Assessment in Complex Terrain

Daniel Cooper

Our objective is development of reliable and useful risk-assessment methods for problems involving the release of atmospheric contaminants. These methods require a combination of quality and simplicity. Quality means accurate and timely estimates of the likely transport trajectories and the dilution, deposition, and transformation of the material during travel. Simplicity means user-friendliness

and ability to implement the estimates with available computing tools.

The development of a micro- and mesoscale, convective, turbulent atmospheric model is well underway. Some initial testing has been performed with very promising results. We used data acquired by the Raman water-vapor lidar showing plume structure over the ocean as a test for validation of the model. Initial results

are very promising, including the ability to model 2- to 5-m structures in the surface layer of the atmosphere for the first time. Furthermore, the model appears to give the structural information observed by the lidar.

The biggest hurdle for the model is the improved code development required for the model to operate on workstation computers, since the present software requires extensive mainframe time. The next step is to improve the model and perform a complete evaluation of the model's ability to simulate complex plume dynamics in the surface-atmosphere interface.

Reservoir Enhancement on the Impermeable Margins of Productive Geothermal Fields: Integrated Resource Development and Management

James Albright

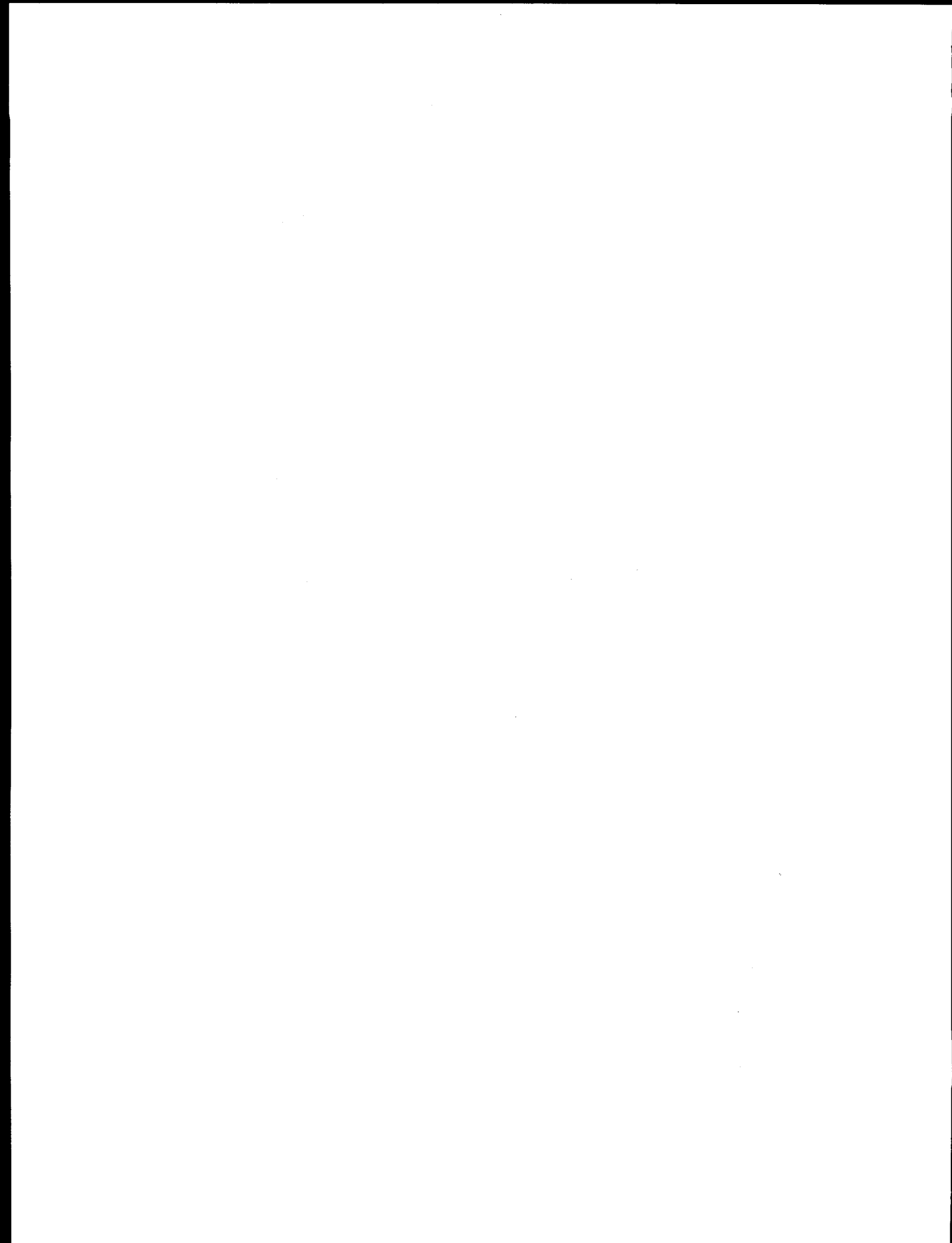
The objective of our project for the past year was three-fold. First, we wanted to identify, collaborate, and partner with members of the geothermal industry in evaluating the application of microseismic mapping technology for assessing the role of fracture permeability in developing and managing geothermal production fields. Second, we planned to prepare a proposal for submission to DOE for the evaluation and assessment of microseismic mapping technology. Third, we intended to reassemble a borehole seismic instrumentation package used in research at Los Alamos 10 years ago and retrofit it

with contemporary electronics and sensors. This package would then be used to conduct assessments of the mapping hardware in producing fields.

In June 1996 in Santa Rosa, California, we introduced the potential for microseismic mapping to representatives of the geothermal industry at a DOE-sponsored workshop on "Subsurface Permeability Detection and Mapping." Representatives from 80% of the major producers attended the workshop. We identified three potential industrial collaborators, visited their geothermal fields, assessed the reservoir development

and management needs, and developed work plans. Two of the collaborators accepted our invitation to participate in preparing a proposal for the evaluation of the technology. We submitted this proposal to DOE in September 1996.

In the past year, we also designed the seismic instrumentation package. We reassembled the package from salvaged parts, machined and fabricated missing mechanical parts, designed and fabricated improved electronics circuitry, and procured and installed state-of-the-art sensors. We tested the entire package in a high-temperature well and deemed the instrument fit for service.



Nuclear and Particle Physics

Disposition of Plutonium as Nonfertile Fuel for Water Reactors

Kenneth Chidester

In this project, we are studying the potential for reducing global plutonium inventories by creating special fuels, especially nonfertile fuels, for burning in conventional reactors. Our project continued to build upon the initial investigations of nonfertile fuels and concentrated on examining evolutionary mixed-oxide (EMOX) fuels consisting of the mixed oxides urania, plutonia, and a nonfertile component (currently, calcia-stabilized zirconia). The nonfertile component replaces some of the fertile uranium, lowering the amount of plutonium produced through breeding and resulting in a net destruction—over the irradiation cycle—of plutonium in the fuel. We performed detailed reactor physics calculations to determine the behavior of the EMOX fuel under a variety of parameters. We also conducted fabrication experiments to determine the feasibility of using standard, commercial processes for fabricating nuclear fuel to produce EMOX fuel with the desired compositions.

The results of the calculations indicate that net reduction of core-averaged plutonium inventories can be accomplished using plutonium loadings of greater than 6% (PuO_2 in UO_2 - PuO_2) with a nonfertile fraction of 30% (amount of fuel that is the nonfertile component). The nuclear reactor is loaded with a one-third core

of EMOX fuel (the other two-thirds contains standard low-enriched uranium fuel). Loading a core entirely with EMOX lowers the plutonium-loading requirement to less than 3%. Plutonium destruction rates increase with increasing plutonium loading and an increasing core fraction of EMOX. Additionally, EMOX exhibits reactivity coefficients nearly identical to those of standard MOX.

We used the solid-state reaction method to fabricate a number of nonfertile and EMOX fuel pellets of varying compositions. The source of reactor fuel was PuO_2 derived from the hydride-dehydride process for converting weapons-grade plutonium metal to oxide. Specifically, we fabricated a nonfertile fuel with a composition of PuO_2 (2.69 wt %), ZrO_2 (87.19 wt %), and CaO (10.12 wt %). The nonfertile fuel was sintered to 89.7% of theoretical density. In addition, we fabricated an EMOX fuel with a composition of PuO_2 (10.97 wt %), UO_2 (83.94 wt %), and ZrO_2 (4.63 wt %). The EMOX fuel was sintered to 96.8% of theoretical density. No fabrication difficulties were encountered.

Publications

Beard, C.A., J.J. Buksa, et al., "Development of Evolutionary Mixed Oxide Fuel," *1996 ANS/ENS Winter Int. Meeting Trans.* **75**, TANSO 75 1-490 (1996).

Buksa, J., S. Eaton, and J. Toevs, "Disposition of Plutonium as Mixed Oxide Nuclear Fuel," *Fourth Int. Conf. Nucl. Eng. (ICONE-4)* **4**, 453 (1996).

Eaton, S.L., C.A. Beard, and J.J. Buksa, "Evolutionary Mixed Oxide Fuel Performance in Pressurized Water Reactors," *1996 ANS/ENS Winter Int. Meeting Trans.* **75**, TANSO 75 1-490 (1996).

Ramsey, K.B., and H.T. Blair, "Fabrication of a Non-Fertile Fuel for the Disposition of Weapons Plutonium," *Fourth Int. Conf. Nucl. Eng. (ICONE-4)* **4**, 499 (1996).

Ramsey, K.B., and K. Chidester, "Fabrication of Non-Fertile and Evolutionary Mixed Oxide Fuels," *1996 ANS/ENS Winter Int. Meeting Trans.* **75**, TANSO 75 1-490 (1996).

An Ultracold Neutron Facility at the Manuel Lujan Jr. Neutron Scattering Center

Thomas Bowles

Ultracold neutrons (UCNs) are neutrons whose wavelengths are so long that they can undergo total internal reflection from a variety of materials. This makes it possible to confine UCNs in a bottle for more than 100 s, making a compact source for use in fundamental physics research.

A UCN capability is seen as an essential component if Los Alamos is to execute a strong and ongoing experimental program that would be among the world's foremost in fundamental neutron physics. This project is intended to develop and demonstrate a first experimental UCN source at the Manuel Lujan Jr. Neutron Scattering Center (MLNSC). This experimental source will be based on a Doppler-shifted, Bragg-scattered source and will use a rotor to select beam pulses from the accelerator.

The UCN source uses Flight Path 11 at MLNSC. A guide tube transports the cold neutrons out to the UCN converter, which is a set of mica crystals on the end of a rotor that rotates in synchronism with the beam pulse rate (20 Hz). UCNs are produced at the rotor and pass through a shutter to be transported by the guide

tube to the experiment. A UCN bottle with filter plates at the ends has been constructed to allow a differential measurement of the UCN velocity spectrum.

Some of our accomplishments this year were the installation and alignment of the guide tube and shutter assembly on Flight Path 11; detailed calculations of the shielding and the shielding design, procurement, and installation; tests of the algorithms for the phasing of the rotor-drive motor to the 400-m/s cold neutrons from the MLNSC liquid hydrogen source; and the assembly and testing of the rotor system, UCN guide tubes, and UCN bottle. Some small modifications to the system to improve operations are currently under way.

Other accomplishments were the installation of the instrumentation for safe operation and monitoring of the system; measurements of the reflectivity and mosaic spread of the mica crystals used in the UCN source; design and building of the crystal package using the parameters obtained from Monte Carlo calculations; and detailed Monte Carlo calculations

of the predicted UCN rate using measured parameters as input. These calculations agree well with our analytical predictions of the UCN rates. More-detailed Monte Carlo and analytical calculations are now under way to better understand the microscopic production processes.

We have also assembled the entire system on the beam line. The system includes the source, monitoring equipment, shielding, and data acquisition electronics and the UCN guide, bottle, filters, and detector. We are waiting for the new liquid hydrogen source to become available at the MLNSC to start the first experimental measurements.

Publications

Seestrom, S.J., T.J. Bowles, et al., "Plans for an Ultra Cold Neutron Source at Los Alamos" (Tsukuba, Japan, Hadron Project Workshop—Nuclear Physics and Fundamental Physics with Neutrons, March 1996).

Seestrom, S.J., T.J. Bowles, R. Hill, et al., "Development of an Ultra Cold Neutron Source at the Los Alamos Spallation Source" (to be published in *Proc. 14th Int. Conf. Appl. Accel. Res. Ind.*).

Seestrom, S.J., T.J. Bowles, R. Hill, et al., "Development of an Ultra Cold Neutron Source at MLNSC" (to be published in *Proc. Int. Conf. Appl. Nucl. Tech.*).

Measurement of Fissile Material in Spent Fuel and Alternate Nuclear Materials

Mark Pickrell

We investigate neutron interrogation methods for measuring spent fuel against high-radiation backgrounds. Two applications of these methods are the measurement of fissile content in spent fuel and the measurement of fissile material in alternate nuclear materials. In our experiments, we used a deuterium-tritium neutron generator developed for borehole logging.

The time control of the neutron signal and the data acquisition electronics that we have developed for and used in the experiments are entirely novel. Instead of using a short neutron pulse, as has been done conventionally, we used a square-wave neutron signal and implemented a digital lock-in amplifier by using a personal computer and digital time

scalers. Compared with conventional techniques, ours yields significantly improved signal-to-noise ratios both from the interrogating neutrons and from the background radiation.

Our new method can be applied to measuring the fissile content and the reactivity of spent fuel for safeguards and safety. Our project led directly to a fully funded program to develop a high-fluence neutron source as the interrogating driver. The high-fluence source will also be used to further improve the signal-to-noise ratio of our measurements.

A Consortium for Biomedical Applications of Single-Molecule Detection

Richard Keller

Our goal is to perform basic research and explore applications in ultrasensitive fluorescence detection technology in collaboration with the University of New Mexico (UNM) and private industry. The Laboratory leads the world in developing techniques for ultrasensitive fluorescence detection in flowing streams. We have demonstrated the detection of individual fluorescent molecules as they are transported through a laser beam. Applications include DNA sequencing, DNA fragment sizing, sensitive assays for randomly generated pharmaceuticals, and assays for ligands to orphan receptors. We anticipate additional applications in the areas of archeology and ecology.

We made significant progress in our approach to DNA sizing; we are now using our flow cytometry approach to size large P1 artificial chromosome clones and extended our sizing range down to 217 base pairs and up to 167,000 base pairs. A small DNA-sizing apparatus has been built and tested. We have developed much faster, more accurate algorithms for single-molecule detection that provide information not previously available. We designed a pressure loading system that reduced sample loading time by a factor of 20. We also refined our measurements on the photobleaching of single molecules of phycoerythrin and submitted the data for publication. In related work, we have developed an assay to find different ligands to promote cell growth in chemotherapy patients. For his contributions

to advancing single-molecule detection, Richard Keller received the Lester W. Strock Award from the Society for Applied Spectroscopy.

In addition to basic research, we developed secondary applications for laser and instrument manufacturers, chemical producers, and testing laboratories.

Publications

Affleck, R.L., W.P. Ambrose, J.N. Demas, et al., "Reduction of Luminescent Background in Ultrasensitive Fluorescence Detection by Photobleaching," *Anal. Chem.* **68**, 2270 (1996).

Ambrose, W.P., R.L. Affleck, P.M. Goodwin, et al., "Imaging Biological Molecules with Single Molecule Sensitivity Using Near-Field Scanning Optical Microscopy," *Exp. Technol. Phys.* **41**, 237 (1995).

Ambrose, W.P., P.M. Goodwin, J. Enderlein, et al., "Fluorescence Photon Antibunching from Single Molecules on a Surface" (submitted to *Phys. Rev. Lett.*).

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Goodwin, P.M., W.P. Ambrose, et al., "Spatial Dependence of the Optical Collection Efficiency in Flow Cytometry," *Cytometry* **21**, 133 (1995).

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Huang, Z., J.T. Petty, B. O'Quinn, et al., "Large DNA Fragment Sizing by Flow Cytometry: Application to the Characterization of P1 Artificial Chromosomes (PAC) Clones," *Nucleic Acids Res.* **24**, 4202 (1996).

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Roslaniec, M.C., C.S. Bell-Prince, H.A. Crissman, et al., "New Flow Cytometric Technologies for the 21st Century" (submitted to *Hum. Cell*).

Wu, M., P.M. Goodwin, et al., "Photochemistry and Fluorescence Emission Dynamics of Single Molecules in Solution: B-Phycoerythrin," *J. Phys. Chem.* **100** (1996).

Cancer Risk Assessment

Bruce Lehnert

Creating new, mechanistically based biotechnological methods for assessing the risk of cancer development in individuals who have been or may be exposed to environmental carcinogens is the objective of this project. Extensive evidence indicates that cancer risk is related to the existence of specific "susceptibility genes" that are heterogeneously distributed among humans. However, an individualized assessment of cancer risk has not been previously possible because of major gaps in understanding the basic mechanisms involved in carcinogenesis.

The scientific focus of this project has been to identify those critical

genes and gene products that render individuals more susceptible to exposures to carcinogens, especially ionizing radiations. The initial specific aims of our mechanistically based effort have been to identify and characterize potential cancer-susceptibility genes that are involved in cell-cycle regulation and DNA repair and to develop advanced flow-cytometry assays for those genes that are candidates for cancer susceptibility. Longer-term goals of the project are to establish relationships between susceptibility gene products and cancer risk and to develop bioassays for assessing the risk posed by the susceptibility genes and gene products.

This year, we have successfully correlated nuclear regulating factors with cell-cycle checkpoints; we have proved that alpha particles, such as those emitted by radon and radon progeny, cause G1 and G2 cell-cycle delays in normal cells; we have found that alpha particles can induce the generation of DNA-damaging extracellular factors that may be exploited as biomarkers of exposure; we have demonstrated that wild-type and mutant p53 differentially alter the cell-cycle and apoptotic responses to DNA damage; and we have demonstrated that poly (ADP-ribose) polymerase is associated with the products of some DNA-repair proteins. Finally, we have demonstrated that phase-sensitive flow cytometry can distinguish between immunofluorochrome-labeled antigens and cellular autofluorescence.

Human Brain Mapping: Experimental and Computational Approaches

Charles Wood

Our project combines novel sensors, data acquisition techniques, and high-performance computing to advance noninvasive brain imaging. The experimental component emphasizes optimization of spatial and temporal resolution of functional brain imaging by combining structural magnetic resonance imaging (MRI) of brain anatomy; functional MRI of blood flow, oxygenation, and volume; and magnetoencephalography (MEG) of neuronal population currents. The computational component emphasizes development of a high-resolution, three-dimensional volumetric model of the brain based on anatomical MRI; this model integrates structural and functional information from multiple forms of brain images.

In the past year, we made four major accomplishments. First, we completed and published the results of our initial experiments using functional MRI (fMRI) and MEG to compare

brain activation under comparable experimental conditions. These experimental comparisons used patterned visual stimulation for activation of striate and extra-striate visual cortex in the two functional imaging modalities. In both fMRI and MEG, we observed multiple foci of activation, which is consistent with predictions of brain activation for nonhuman primates. We are performing additional analyses to determine the precise degree of correspondence between the two activation measures.

Second, we completed and published the results of our MEG studies of retinotopic organization of the human visual cortex. This analysis demonstrated small but systematic departures from the conventional "cruciform" model. These data will form the base for further comparisons of fMRI and MEG.

Third, we made significant progress on developing algorithms and soft-

ware for constrained modeling and integration of anatomical MRI, fMRI, and MEG. These same techniques will be extended to integration with other functional imaging modalities.

Finally, we continued trade-off studies between boundary element models for the electromagnetic inverse problem and the widely used and simpler spherical and spherical-shell models. Boundary element models can, in principle, provide greater accuracy at the cost of increased computational complexity. However, neither the extent of the theoretical gains in accuracy nor the associated degree of additional computational cost have been thoroughly explored.

Publications

Aine, C.J., et al. "Retinotopic Organization of Human Visual Cortex: Departures from the Classical Model," *Cerebral Cortex* 6, 354 (1996).

George, J.S., et al., "Mapping Function in the Human Brain with MEG, Anatomical MRI, and Functional MRI," *J. Clin. Neurophysiol.* 12, 406 (1995).

Universal Biological-Agent Point-Sensor Program Development

Gary Salzman

The three objectives for this project were (1) to upgrade our biology laboratory to Biosafety Level 2 (BL2) and to provide organisms and toxins to investigators in the Life Sciences Division and other Laboratory organizations, (2) to help develop and then to use a DNA-fragment-sizing flow cytometer (here called a microflow cytometer) to determine whether

bacteria can be identified by the mass spectrum of a DNA fragment obtained using a set of restriction enzymes, and (3) to develop flow-cytometric methods for identifying toxins.

This year we completed the BL2 upgrade and obtained 25 microorganisms. We also developed a microflow cytometer for DNA-fragment sizing. The flow cytometer uses a 532-nm,

solid-state laser, a microchannel flow chamber, and a photon-counting detector. We obtained DNA fragments using restriction enzymes and stained the fragments with POPO-3, a dye that is stoichiometric for DNA content. We then analyzed the fragment sample with the microflow cytometer. The response was linearly proportional to DNA content from 384 to 167,000 base pairs. We obtained DNA-fragment spectra from λ -phage DNA and from bacteria artificial chromosomes. We also developed bead-based sandwich assays for botulinum toxins A and B, ricin, and anthrax.

Sensors for Point Detection of Chemical and Biological Warfare Agents

Thomas Zawodzinski

The goal of this project was to develop sensors that detect airborne chemical warfare (CW) agents. During this year we progressed in demonstrating electrochemical sensors for CW agents and in developing surface coatings for surface acoustic wave (SAW) and optical sensors for CW agents. In addition to sensing CW agents, we can also chemically modify, and thus destroy, CW agents using either our electrochemical or our SAW and optical technologies.

We demonstrated electrochemical sensors for quantifying HCN (a blood agent) and have also demonstrated a possible electrochemical approach for quantifying sulfur mustards. Using both enzymatic and enzyme-mimicking catalytic sensors, we could sense HCN in the part-per-billion range. The enzyme-mimicking catalytic approach involves replacing the enzyme

with an organometallic complex that mimics the enzyme function. This approach adds considerable robustness to our sensor while retaining the amplification from electrocatalytic reactions. The HCN sensors are also reversible. We are preparing several patent applications stemming from this work.

Our specific goals for the SAW and optical sensors were to (1) develop new self-assembled linker layers to enhance thin-film densities and stabilities, (2) develop new approaches to multilayer thin films for enhanced sensitivity, and (3) measure the SAW response of cyclodextrin (CD) and calixarene (CA) thin films to CW-agent simulants.

First, we developed and tested new, high-density, well-ordered linker layers based on bifunctional self-assembled thin films. These linker

layers resulted in an approximately 25% improvement in the density of reagent molecules. This higher density led to increased sensitivity and more stable films. We also used these new linker layers as reference films in SAW measurements. Second, we developed a new polyelectrolyte deposition method to quickly prepare multilayer thin films with control at the molecular level. So far, we have tested this approach on CA and nickel phalocyanine thin-film reagents and will soon test it on CD reagents. These thin films are quite stable and reproducible. We also developed a new sol-gel approach to prepare multilayer films with excellent control of the reagent chemistry. New multilayer films prepared in this manner have shown excellent sensitivity and stability. Third, we began testing CD and CA monolayer films against CW-agent simulants. We also developed a test bed for Zeeman interferometry and initiated tests using our CD and CA thin films.

Molecular Medicine for the 21st Century: A Computational Basis for Design and Critique of Vaccines and Therapeutics

Alan Lapedes

The kissing-loop RNA motif, in which the loops of two stem-loop structures base-pair with each other, is thought to modulate steps in the life cycle of retroviruses such as HIV (see accompanying diagram). Using an RNA-folding protocol developed for this project, which takes into account information on possible base pairings and structural constraints resulting from connectivity requirements, we are studying the folding of a potential kissing-loop motif in HIV. Specifically, we are modeling the structure and the flexibility of this motif, and we have worked out three possible structures with low conformational energies (see accompanying figure showing molecular models).

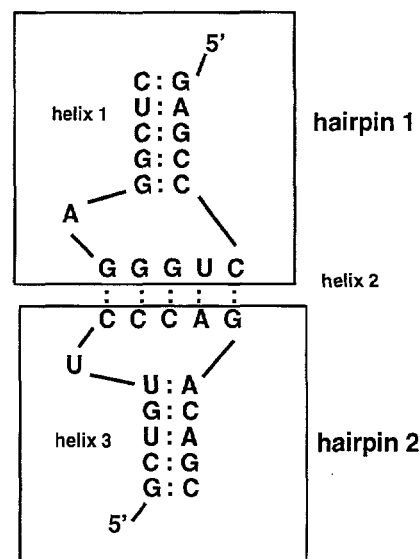
Following on our earlier work, in which we analyzed correlated mutations (also known as nonindependent mutations) in the V3 loop of HIV, we have developed an evolutionary model that incorporates these mutations at

different positions in model sequences. (A correlated mutation is a mutation at one site that affects a mutation at another site.) Our evolutionary model takes into account how the phylogenetic tree affects the analysis of mutations, and it shows a higher correspondence of correlated positions with structurally adjacent positions in the model than do previous analyses.

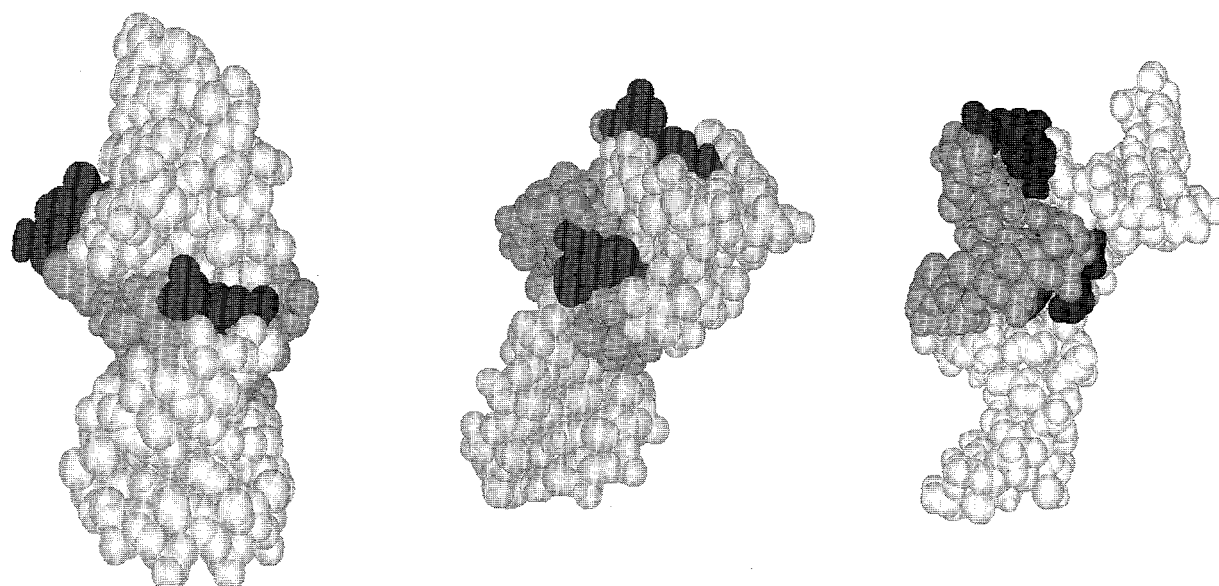
Furthermore, using patient data and simple models, we have begun analyzing and have published the first quantitative estimates of the dynamics of HIV in vivo. We found that 10 billion viral particles are produced and cleared each day in a typical mid-stage AIDS patient and that the vast majority (99%) of virus is produced by cells that live only about 1.5 days. These estimates suggest that if HIV replication can be completely stopped by potent drug combinations, then all HIV and infected cells might be eliminated from the body after two to three years of treatment.

Publications

Perelson, A.S., A.U. Neumann, M. Markowitz, et al., "HIV-1 Dynamics In Vivo: Virion Clearance Rate, Infected Cell Lifespan, and Viral Generation Time," *Science* **271**, 1582 (1996).



The sequence and secondary structure of HIV TAR-TAR* kissing-loop motif.



Three predicted structures of the HIV TAR-TAR* kissing-loop motif. Helices 1 and 2 are shown in light gray, and helix 3 is in medium gray. The two single-stranded loops (p-A-p, p-U-p) are plotted in dark gray.

Distributed Telemedicine for the National Information Infrastructure Testbed

David Forslund

TeleMed is an advanced data management tool that uses object-based computing, distributed data repositories, advanced graphical user interfaces, visualization tools, and innovative concept extraction of image information for storing and accessing medical records. More than a standard client/server application, TeleMed has a multitiered architecture in which there are multiple servers between the persistent storage of databases and the clients.

In the original deployment of TeleMed, we used a Sybase product called Gain Momentum for the client because of its powerful multimedia user-interface capabilities. Because the Java programming language was so widely and rapidly accepted on the basis of its portability and its usability on the Internet, we have elected to move away from Gain Momentum.

This year we began the transition from the Gain Momentum client to a Java-based client, extended the infrastructure to support relational databases, and worked with industry to begin the process of deploying technologies similar to TeleMed throughout the nation. We coordinated the work of several organizations to collaboratively sponsor two workshops on the Master Patient Index for use throughout the healthcare industry. The system was also deployed and tested at the National Jewish Center for Immunology and Respiratory Medicine in Denver, Colorado, and at the National Institutes of Health in Bethesda, Maryland. Our proposal to work with the National Information Infrastructure Testbed was rejected by that organization, which is now called the InfoTest. However, our work in this area has caught the interest of a

potential commercial partner, and the United States Army has given us funding to deploy TeleMed in its various testbeds. We have also worked successfully with Northern New Mexico Community College to find ways of making TeleMed available for rural healthcare, including the award of a two-year grant by the National Telecommunications & Information Administration of the Department of Commerce.

Publications

Forslund, D.W., "What CORBA Can Do: an Example of a New System Developed with Object Technology," *Proceedings: Toward an Electronic Patient Record V* (II), 255 (1996).

Forslund, D.W., and D. Kilman, "The Virtual Patient Record: A Key to Distributed Healthcare and Telemedicine," *First Class Magazine VI* (II), 14 (1996).

Forslund, D.W., R.L. Phillips, et al., "Experiences with a Distributed Virtual Patient Record System," *J. Am. Medical Informatics Association Proceedings Symp. Supple.*, 483 (1996).

Deformable Human Body Model Development

William Wray

Our goal is to develop a realistic, fully accessible, deformable human body model that is applicable to automobile design by integrating existing anthropomorphic dummy models with existing detailed biomechanical component models.

We have conducted extensive study of human body anatomy and mechanics and determined that the critical joints that are sufficiently movable to

require representation in the deformable human body model include the major synovial joints of the upper and lower limbs, the synovial joints of the rib cage, and the cartilaginous joints of the vertebral column.

The major synovial joints of the appendicular skeleton include the ball-and-socket joints of the shoulders and hips and the hinge joints of the elbows and knees. The sternocostal

and costovertebral joints of the rib cage are gliding synovial joints, except for the first sternocostal joint, which is cartilaginous. The cartilaginous joints of the cervical, thoracic, and lumbar vertebrae are of a type called symphysis.

We have developed methods of representing the three types of synovial joints (gliding, hinged, and ball-and-socket) and one type of cartilaginous joint (symphysis) in finite-element codes. These joint representation methods will provide a means for linking detailed biomechanical models to the baseline anthropomorphic dummy models.

Detection and Characterization of Biological-Weapons Agents by Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

Charles Wilkerson

The objective of this project was to develop and demonstrate a field-deployable point sensor, based on matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, to unambiguously identify biological toxins. Specifically, our goals were to (1) develop a MALDI source capable of coupling with either a time-of-flight (TOF) mass spectrometer or an ion-trap (IT) mass spectrometer,

(2) characterize the MALDI source from instrumental and application perspectives, (3) implement methodologies for identifying biological toxins and verifying their structures, (4) critically compare experimental results obtained when the MALDI source is used in combination with a TOF or IT mass spectrometer, and (5) design a field instrument based on

the detection system that produced the highest-quality data.

During this year we constructed instrumentation to perform MALDI-TOF mass spectrometry on proteins. In addition, we wrote and tested data acquisition and analysis software. We successfully detected the proteins gramicidin S (~1150 Da) and bovine insulin (~5300 Da), but technical obstacles prevented us from observing larger species, such as anthrax toxins (80,000–90,000 Da) and botulinum toxin A (~150,000 Da). Over the course of the year, we modified the instrument, continually improving its capabilities. We also modeled the behavior of ions in the spectrometer to help extend our high-mass capabilities.

Novel Gene Complex Structure Determination by Neutron and X-Ray Scattering

Joe Gatewood

There are in excess of 200,000 genes in each cell in the human body. Most of these genes are inactivated while specific genes remain functional. The packaging of genes into higher-order chromatin is a fundamental factor in determining gene activity. The basic unit of chromatin is the core particle, which consists of DNA wrapped around a protein assembly of the four core histones. Two copies of each of the four core histones combine to form a protein octamer, which binds 146 base pairs of DNA. A fifth linker histone (histone H1) interacts with DNA extending from the core particle to form the nucleosome. The proteins in this complex are similar in organisms ranging from mouse to man. The core histones consist of "major" and "minor" variants. The minor variants constitute less than 15% of the histones in somatic cells.

We have successfully isolated "operative" chromatin containing exclusively the minor histone variants. Histone H1 is quantitatively missing from operative chromatin. One of the aims of this project was to determine the proteins responsible for stabilizing operative chromatin. This chromatin is stabilized by the microtubule proteins tau and tubulin. Another goal of this project was to characterize the structure of operative chromatin nucleosomes. Using solution scattering, we examined nucleosomes containing the minor variants and demonstrated that these particles are structurally distinct from nucleosomes containing the major variants. The unusual structure and stabilization of operative chromatin by microtubule proteins provides a possible mechanism for direct interaction of transcription machinery with specific chromatin domains.

In Situ Bioremediation of Trichloroethylene-Contaminated Groundwater

Nina Rosenberg

Results of bioremediation efforts are typically variable and difficult to predict. An incomplete understanding of the effects of variable site characteristics (notably, soil heterogeneity, indigenous microbial ecology, and contaminant speciation) and the lack of adequate tools that would allow specialists to predict results and measure successful bioremediation strategies have made the implementation of bioremediation more empirical than desired. Our main objective for this project is to develop practical computational tools that will enable us to work with site owners and providers of remediation services in order to solve problems in site-specific design and in performance assessment and implementation of bioremediation strategies for chlorinated solvents, such as trichloroethylene (TCE), in groundwater.

This year, we have accomplished a number of tasks. First, we have conducted an extensive literature review of previous experiments on competition between different types of microbes present in soil and on predation in soil microbe systems. It has become clear not only that predation and competition are present at contaminated sites, but that they also

have a significant impact on the effectiveness of microbial degradation of contaminants. Next, we created a computer code that can be used to characterize microbial metabolism in laboratory-scale bioreactors.

We conducted sensitivity analyses of key biokinetic parameters in a field experiment aimed at the bioremediation of TCE contamination, and then we ranked the parameters. It is known that the degradation of TCE generates by-products that are toxic to the degrading microbes. Our analyses indicated that TCE toxicity was, in fact, the most important parameter. We also analyzed soil heterogeneity through homogenization theory. The naturally occurring heterogeneity in soils has not been included adequately in previous modeling studies of bioremediation; that is one major reason for such studies not to have been sufficiently accurate. In computational models, the total volume of soil encompassed by a field site is represented by a grid of small boxes, and a single value is used for soil properties within each box. As a result, subgrid-scale variability is completely smoothed away. However, in reality, subgrid-scale heterogeneity can

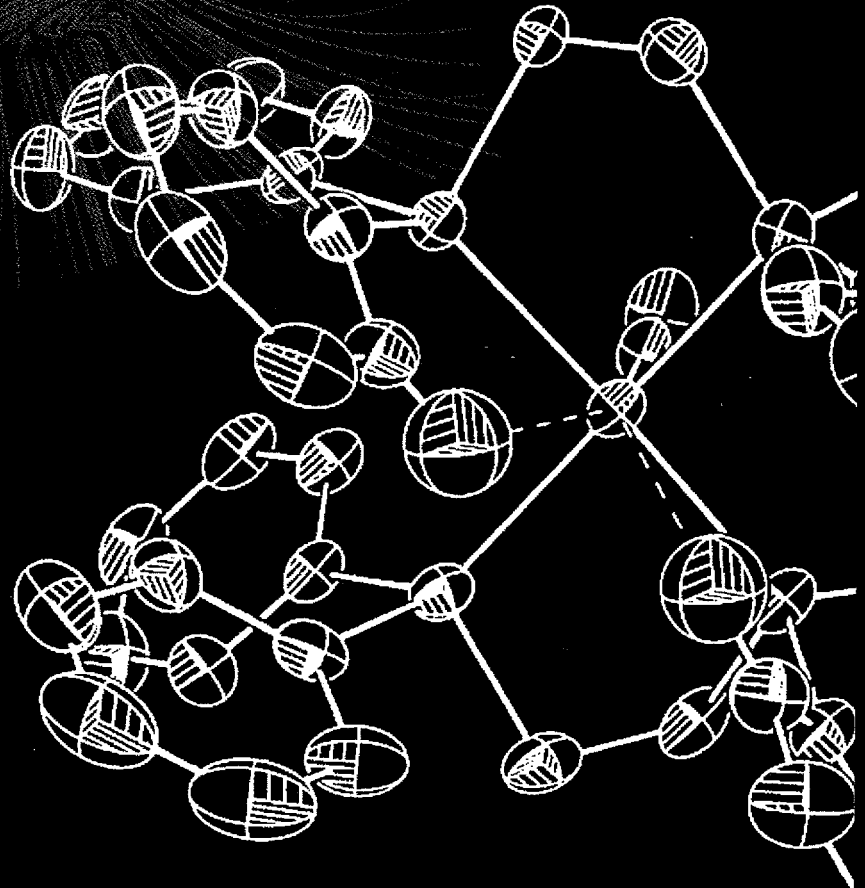
modify the flow field, and thus it can strongly affect the chemical environment of the microbial population. Our model removes part of this source of error through application of homogenization theory. Homogenization theory determines an equivalent tensor to represent subgrid-scale properties. Computational experiments indicate this is a significant improvement over the former use of single scalar quantities within grid boxes.

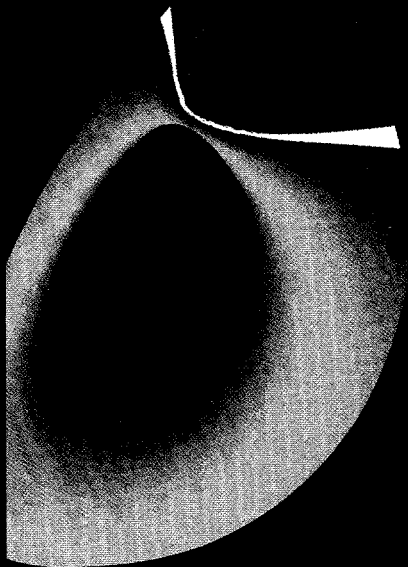
Finally, we have prepared several manuscripts for submission to professional journals and have submitted a proposal to the Environmental Management Science Program (EMSP) competition. Our proposal was closely tied to a project on the genetic engineering of bacteria to more efficiently degrade TCE. Although our proposal made it to the last round, it was not funded. However, reviews were favorable, and we plan to resubmit an improved proposal for the next round of the EMSP competition, as well as for the upcoming Natural Accelerated Bioremediation call.

Publications

Travis, B.J., and N.D. Rosenberg, "Modeling In Situ Bioremediation of TCE at Savannah River" (submitted to *Environ. Sci. Technol.*).

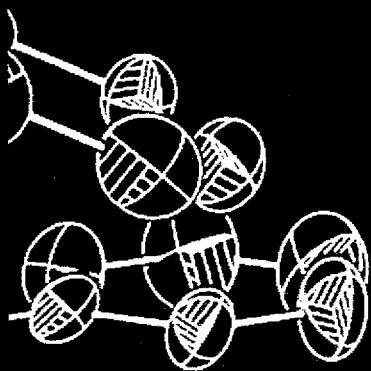
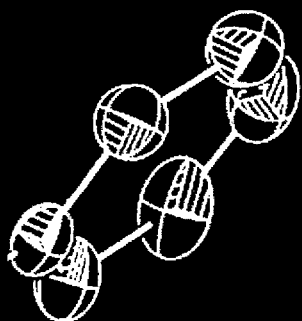
Vanderberg-Twary, L., K. Steenhoudt, B. Travis, et al., "Biodegradation of Paint Stripper Solvents in a Modified Gas Lift Loop Bioreactor" (to be published in *Biotechnol. Bioeng.*).





1 9 9 6
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Index of Principal Investigators



Index of Principal Investigators

A

Abdallah, J. Jr. 72
 Albers, R. 157
 Albright, J. 285
 Alcouffe, R.E. 194
 Altherr, M. 119
 Arthur, E.D. 187
 Aubrey, J. 241
 Avens, L. 266

B

Balatsky, A. 156
 Baldrige, W.S. 189
 Barlow, D. 174
 Barrett, C. 274
 Benage, J. 40
 Benjamin, R. 171
 Berendzen, J.R. 129
 Bhatia, T.S. 177
 Bhattacharya, T. 111
 Bigio, I. 25, 127, 129
 Birn, J. 92, 218
 Bishop, A. 70, 161, 191, 204
 Booth, T.E. 190
 Borovsky, J. 99
 Bourke, M.A.M. 147, 152
 Bowles, T. 288
 Bowman, J.D. 103
 Bradbury, E.M. 126
 Brainard, J. 235, 237, 267
 Breshears, D.D. 93
 Brown, D.L. 61
 Brown, M. 276
 Buescher, K. 273
 Burns, C. 47
 Bystritskii, V.M. 170

C

Camassa, R. 65
 Campbell, I. 159, 249
 Campbell, L. 168
 Carlson, J. 105
 Carlsten, B. 43
 Casperson, D.E. 94
 Cerutti, J.H. 275
 Chamberlin, R.M. 59
 Chen, D. 118
 Chen, S. 67
 Chen, W. 66
 Chidester, K. 287
 Clark, T. 41
 Clements, B.E. 155
 Cline, M. 232
 Cobble, J.A. 44
 Collins, L. 71
 Coogan, J. 259
 Cooke, D.W. 9
 Cooper, D. 285
 Cort, B. 140
 Cram, L.S. 118, 226
 Cranfill, C.W. 188
 Cremers, D. 23

D

Davis, H.A. 26
 Day, R.D. 256
 Devlin, D. 146
 Doering, C. 194
 Doggett, N. 227
 Donahue, J. 262
 Donohoe, R. 21, 185
 Doolen, G. 167
 Drake, 278
 Dreicer, J.S. 279
 Dunand, D.C. 152
 Dye, R. 14, 242
 Dyer, R.B. 121

E

Earl, W. 51
 Early, J. 261
 Ecke, R. 202
 Eckert, J. 148
 Elling, J.W. 23
 Elliott, S. 98
 Epstein, R. 15, 211

F

Faber, V. 203
 Faehl, R.J. 41
 Farnum, E. 29
 Farrar, C.R. 31, 171
 Fasel, J. 199
 Fazio M., 37
 Fearey, B. 281
 Federspiel, F. 108
 Fenimore, E. 83
 Fitzsimmons, M. 154
 Flynn, E. 169
 Forehand, H. 273
 Forslund, D. 293
 Frauenfelder, H. 233, 236
 Freyer, J.P. 123
 Funk, D.J. 73, 172
 Funsten, H.O. 75, 250, 256

G

Garcia, A. 122
 Gary, S.P. 81
 Garzon, F. 35
 Gatewood, J. 294
 Gavrilov, E. 68
 Gerstl, S. 208, 212, 214
 Glatzmaier, G. 82, 207
 Goff, F. 88
 Goodwin, E. 116
 Gosling, J. 85

Gosnell, T.R. 33, 74
Gottesfeld, S. 25
Gubernatis, J. 193, 198, 200, 201
Gupta, G. 120, 228
Gupta, R. 114
Guthrie, G. 251
Guzik, J. 86

H

Hahn, H. 199
Haight, R. 108
Hamkalo, B. 226
Hammel, P.C. 27, 151
Haschke, J. 60
Hasslacher, B. 62
Haussler, D. 232
Hawley, M. 144
Hayden, F.G. 127
Heffner, R. 147, 243
Hemberger, P. 255
Henriksen, A.D. 278
Henson, B. 58
Hermes R., 59
Hersman, L. 230
Hickmott, D.D. 78, 248
Hills, J. 95
Hime, A. 110
Hixson, R. 11
Hjelm, R. 140, 227
Hoffbauer, M. 14
Hoffman, C. 108
Holm, D.D. 30, 62, 63
Houts, M. 255
Howe, P.M. 243
Howell, J.A. 251
Huang, J. 155
Hubbard, K. 18
Hughes, R. 31, 34
Hyman, J. 64, 66

J

Jacobson, A. 91
James, B. 249
Jarvinen, G. 245, 268
Jen, E. 69
Jia, Q. 153
Johnson, P. 83
Johnston, R. 30
Jones, E. 76

K

Kao, C.-Y.J. 80, 213
Kapustinsky, J. 27
Keller, C. 216
Keller, R. 229, 289
Kendall, R.P. 283, 284
Kinnison, W. 104
Kirkpatrick, R. 180
Kocks, U.F. 143
Koskelo, A. 79
Kraus, R. 36
Kubas, G. 54

L

Lackner, K. 34, 183
Laflamme, R. 99
Lai, C.-C. 91
Lamartine, B. 36
Lapedes, A. 232, 292
Lehnert, B. 290
LeSar, R. 275
Lewis, G. 250, 254
Lewis, P. 247
Li, D. 20, 53
Lomdahl, P. 192
Lowe, T.C. 146

M

Macinnes, M. 183, 230
Mack, J. 247
Madland, D. 111
Maggiore, C. 179
Mainieri, R. 35
Maley, M. 160
Margolin, L. 188
McBranch, D. 45, 159
McComas, D.J. 75
McDonald, T. 253
McNaughton, M.W. 109
Migliori, A. 19
Miller, W. 100, 102
Milonni, P. 74
Mitchell, T. 163
Morel, J. 61, 189
Morris, C. 175, 177
Mosteller, R. 201
Mottola, E. 112, 198
Munson, C. 262

N

Nguyen, D.C. 40
Niederauer, G. 254

O

Ott, K. 57

P

Paffett, M. 185
Papcun, G. 274
Park, M.S. 119, 231
Parkin, D. 149
Pearson, J. 130
Peng, J.-C. 109
Perelson, A. 127
Perry, F. 95
Petrovic, J. 244
Phillips, D.R. 213
Picard, R. 195
Pickrell, M. 288
Poling, D. 192
Prather, K.A. 184
Pratt, L. 117
Preston, D. 168

Q

Quinlan, D. 67

R

Rider, W. 196
Roberts, J. 135, 145
Roberts, R.S. 35
Robinson, B.A. 80
Robinson, J.M. 84, 184
Robinson, R. 142, 223
Rosenberg, N. 295
Rosocha, L.A. 170, 265
Ryne, R. 182

S

Saltzman, J.S. 65, 193
Salzman, G. 291
Sauer, N. 52
Scheuer, J. 260
Schiferl, D. 90
Schiferl, S. 18
Schmidt, D. 24
Schmidt, S.C. 56
Schoenborn, B. 120
Schroeder, N. 267
Schultz, J. 284
Schwarz, R.B. 138
Scovel, J. 63
Scripsick, R. 137
Seestrom, S. 179
Shankland, T. 220
Shashkov, M. 69
Sheffield, R. 178
Shi, N. 136
Sickafus, K.E. 10
Silks, L.A. 46, 116
Sinnis, C. 113
Smith, B.F. 57, 270
Smith, D. 19
Smith, G. 137, 149, 226
Soderquist, S.D. 173
Solem, J. 244
Sparks, W. 81
Steckle, W.P. 15
Stevens, M. 154, 241
Strauss, C.E.M. 71
Stringfield, R. 271
Suszcynsky, D. 78
Swanson, B. 150
Sze, R. 32

T

Taylor, A. 28, 38, 252
Terwilliger, T. 121, 122
Thode, L.E. 39
Thoma, D. 12
Thompson, J. 209
Thompson, J.D. 139, 158, 242
Tolmie, D. 68
Torney, D. 124, 234
Trehwella, J. 115, 225, 234
Tumas, W. 48, 269

U

Ullmann, J. 108
Unkefer, C. 128

V

Venneri, F. 174
Vieira, D. 106
Voter, A. 50

W

Wadlinger, E. 260
Warren, M. 85
Watkin, J. 55
Wesse, F.J. 170
West, G. 104
White, A. 200
Wilkerson, C. 294
Williams, M. 276
Wills, J. 142
Winske, D. 102, 210
Wood, C. 117, 290
Woodruff, W. 52, 60, 225
Wray, W. 293
Wysocki, F. 42

Y

York, R. 248

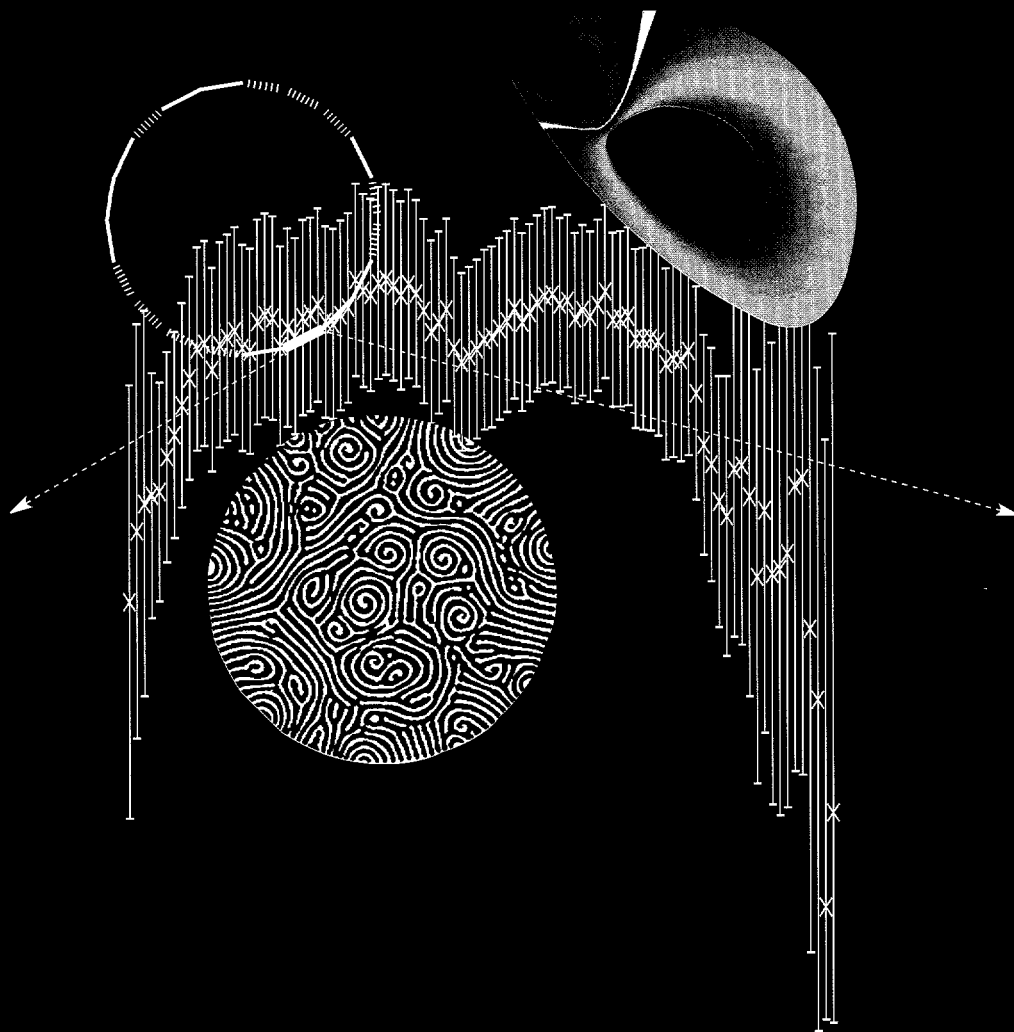
Z

Zaera, F. 185
Zawodzinski, T. 51, 291
Zhu, Y.T. 16
Zurek, W. 96, 98
Zweig, G. 64

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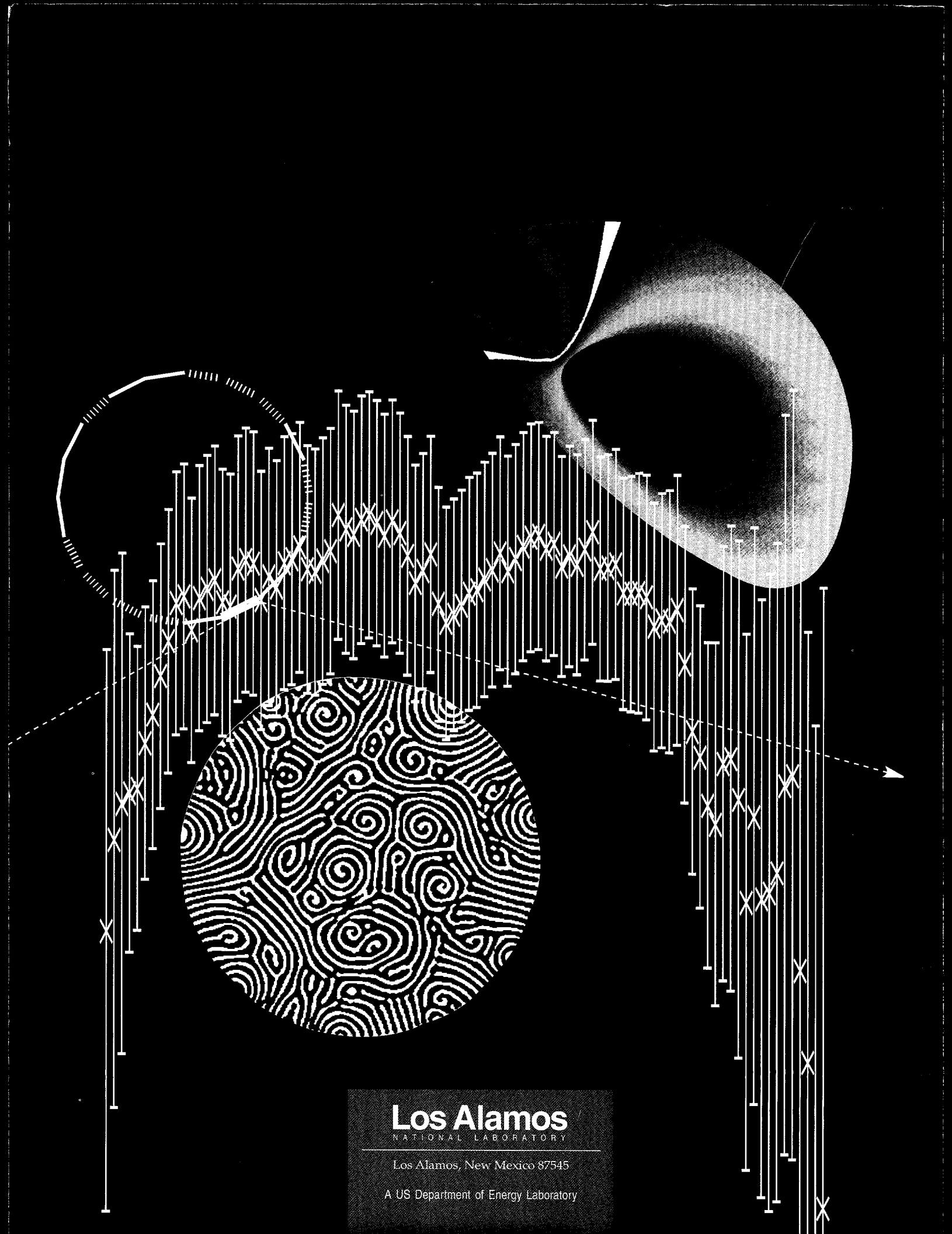
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Clockwise from upper right:

- Accretion disk around a rotating black hole (W. Miller, "Accretion onto Black Holes: The Power-Generating Mechanism").
- Diffusion image of helium-3 gas at thermal equilibrium (D. Schmidt, "Nuclear Magnetic Resonance Imaging with Hyperpolarized Noble Gases").
- Optical shadowgraph of the spiral defect chaos state in thermal convection (R. Ecke, "Self-Organization and Pattern Formation").
- Plasmid for expressing fusion proteins (J. Trewella, "Biotechnology Approaches to Stable-Isotope Labeling for Biomolecular Structure/Function Studies").



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