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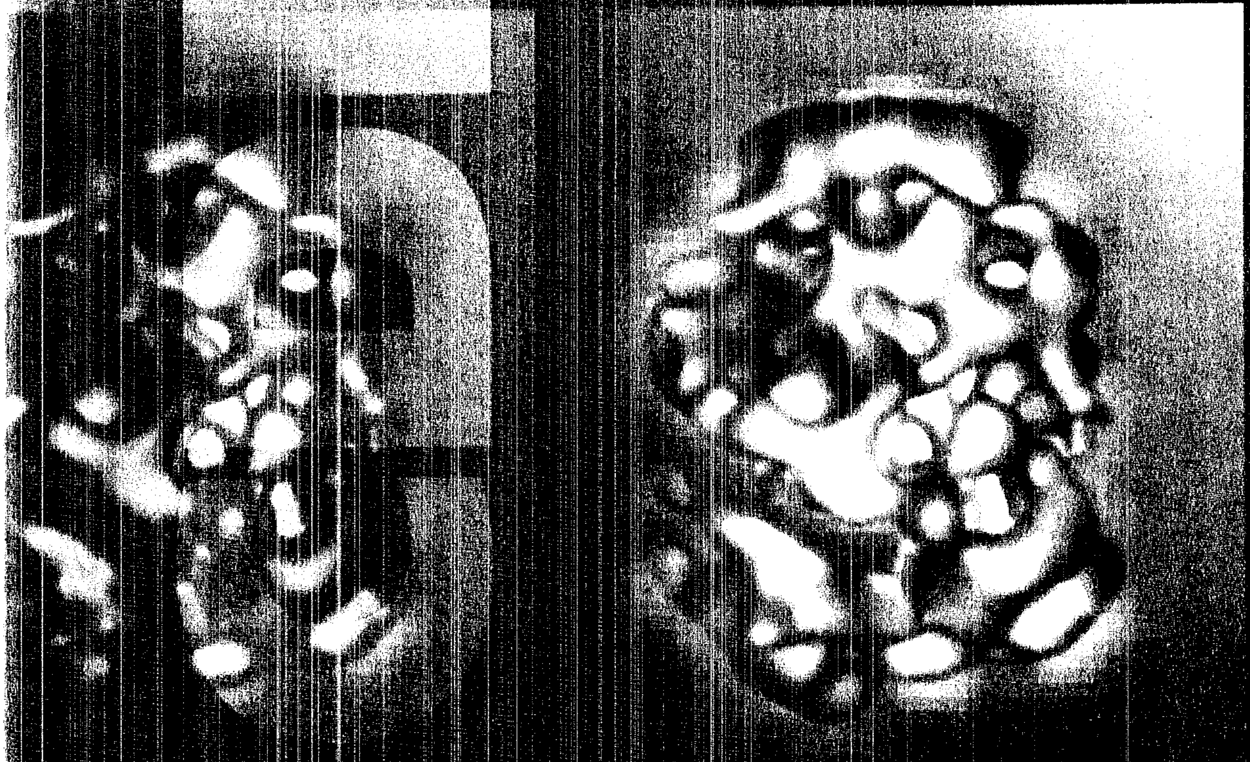
Submitted to: Annual Report for DOE and UC

Los Alamos
NATIONAL LABORATORY

University of California

Directed Research and Development (UCDRD) Activities for Fiscal Year 1998



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University of California Directed Research and Development (UCDRD) Activities for Fiscal Year 1998

Compiled by
University of California Coordination Team

Submitted to

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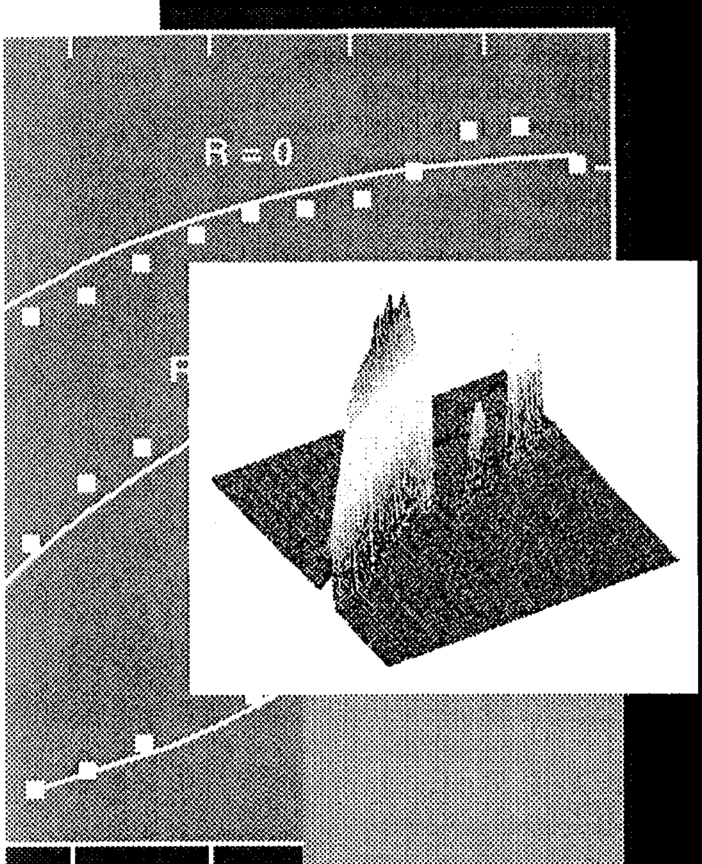
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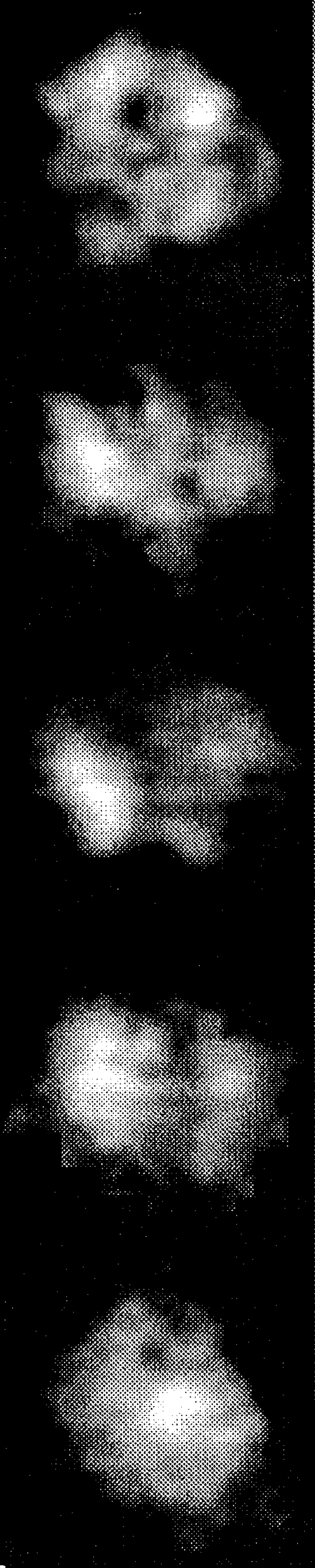
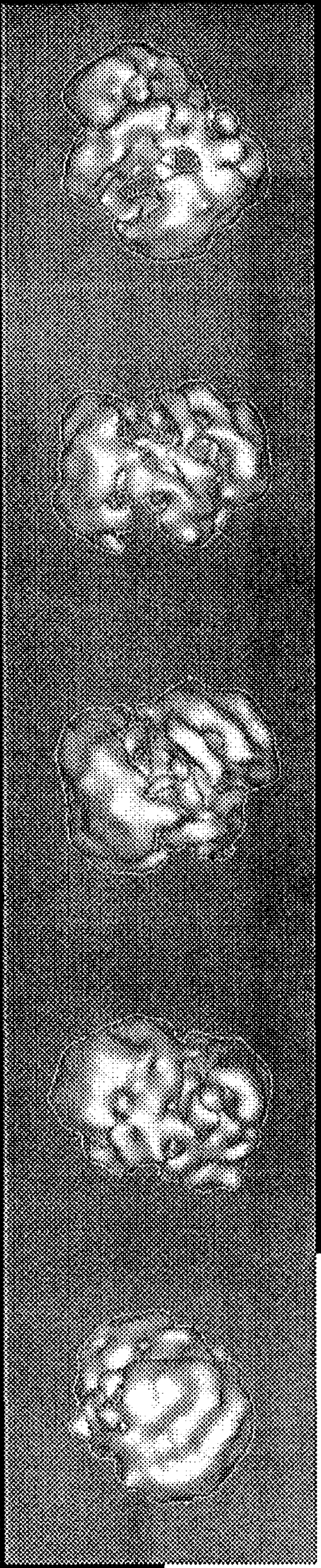




Overview of UCDRD Program Objectives, Components, and Activities

Program Objectives

This report describes FY 1998 University of California Directed Research and Development (UCDRD) activities at Los Alamos National Laboratory carried out in collaboration with campuses of the University of California and with universities in New Mexico. The report is prepared by Los Alamos for the University of California (UC) and the Department of Energy (DOE). Funds for UCDRD activities are derived from a portion of the fee paid to UC for managing the Laboratory. After deduction of unallowable costs incurred by the Laboratory and as an incentive to avoid unallowable costs, these funds are returned to the Laboratory to be used at the Laboratory Director's discretion for research and research-related activities. The Director is using UCDRD funds to enhance collaborations with UC campuses and universities in New Mexico and to strengthen selected areas important to the Laboratory. This use of UCDRD funds is deemed to be beneficial to DOE, Los Alamos, UC, and New Mexico universities.

Program Components

The UCDRD activities at Los Alamos, which are administered by the UC Coordination Team of the Science and Technology Base Program (STBP) Office, are currently supported under the following five components:

- The Collaborative UC/Los Alamos Research (CULAR) Program funds small research projects between Los Alamos and the UC campuses, specifically in the area of three Los Alamos core competencies: bioscience and biotechnology, earth and environmental systems, and materials science.

- The UC Research Partnership Initiatives (UCRPI) Program fosters the development of joint Los Alamos–UC campus research capabilities that have the potential for external funding and significant research advances.

- The New Mexico Universities Collaborative Research (NUCOR) Program is designed to strengthen research collaborations with New Mexico universities (New Mexico Highlands University, New Mexico State University, New Mexico Institute of Mining and Technology, and University of New Mexico), specifically in the areas of satellites and remote sensing, earth and environmental systems, and materials and advanced manufacturing.

- The New Mexico Research Partnership Initiatives (NMRPI) Program fosters the development of joint Los Alamos–New Mexico campus research capabilities that have the potential for external funding and significant research advances.
- The Visiting Scholar Program funds Los Alamos staff in research and related teaching at UC campuses and UC faculty in research at Los Alamos for a period of six to twelve months.

Collaborations with the UC campuses began in FY 1994. Collaborations with New Mexico universities were added to the UCDRD program in FY 1997; the first allocations of funds were made late in the FY 1997.

Following this section are five sections containing short descriptions of the current UCDRD projects under the CULAR, UCRPI, NUCOR, NMRPI, and Visiting Scholar components. These sections contain information about project personnel and funding; reports describing the projects and their technical progress; and lists of resulting publications, presentations, patents, and awards. An index of investigators is also included at the end of the report.

Program Activities

Statistical Information. Substantial growth has occurred in UCDRD activities since our last annual report. The total number of UCDRD projects has grown from 15 in FY 1995 to 42 in FY 1996 and 77 in FY 1997. The actual number of projects in FY 1998 was 81; however, 8 of these were started so late in the fiscal year that including them in the statistics and requiring progress reports were not feasible. The growth in the number of projects is reflected in the number of people associated with the UCDRD projects and in the number of program-related publications and presentations. In addition to showing the number of projects, Figs. 1, 2, and 3 show, respectively, the demography of people associated with UCDRD projects, the resulting publications, and the related presentations, patents, and awards for FYs 1995–1998.

A few words of explanation will help the reader evaluate the basis and validity of the statistical information shown in these figures. The accuracy and completeness of the information provided depends on the more than 300 collaborators involved with the many projects. For example, the Coordination Team requested information about the number of collaborators involved with each project, but because the degree of involvement is difficult to define and measure and likely different for each project, the task of definition and collaborator identification was left to the principal investigators. We believe that, as a result, the reported number, although impressively large, is an underestimate of the true number of intellectually involved collaborators.

In addition, an accurate count of publications that result from UCDRD-supported research is hampered by timing: first, an unavoidable time lag occurs between doing research and having the results appear in print, especially when peer review is involved; and, second, once the time of UCDRD funding ends, official contact between the Coordination Team and the growing number of principal investigators also ends.

We believe that, as a result, some publication data are uncounted so that the number of peer-reviewed publications in print or accepted for publication are underestimated. Therefore, we have begun to provide separate statistics about papers that have been submitted but have not yet been accepted (Fig. 2). To obtain a more meaningful picture of publications and

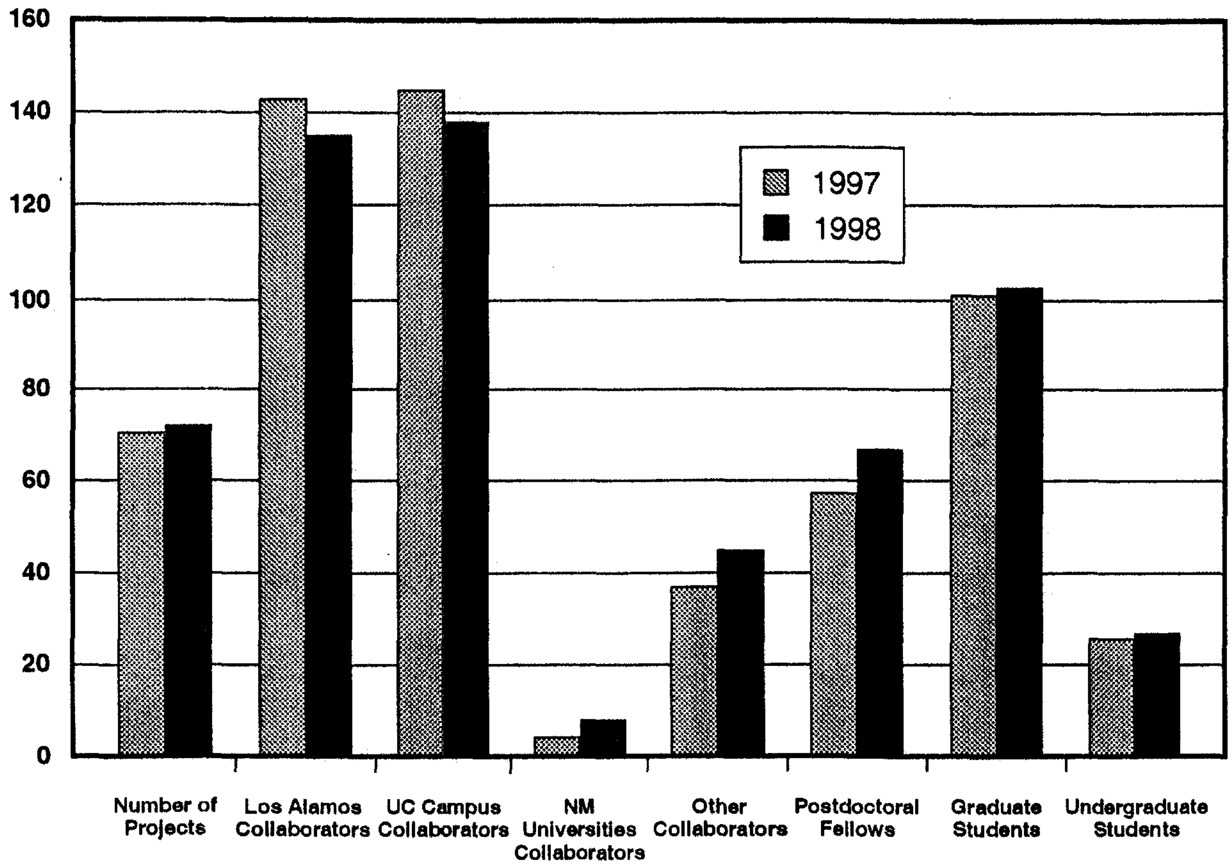


Fig. 1. Number of UCDRD projects and number of UCDRD project personnel for FYs 1997 and 1998. Categories of personnel include the lead investigators at Los Alamos, UC campuses, and New Mexico universities; other collaborators (professional-level personnel at Los Alamos and university campuses); postdoctoral fellows; graduate students; and undergraduate students. These include both full-time and part-time personnel.

presentations, during only the duration of each UCDRD project, would require more careful accounting and time integration of the data by all collaborators than is possible, or even desirable. The time-lag problem is especially serious when it comes to counting patents granted (Fig. 3).

The statistical data in Fig. 1 clearly shows that UCDRD research activities have strengthened collaborative ties between Los Alamos and the UC and New Mexico campuses. As time passes, these ties become much stronger than our annual statistics indicate. Once successful ties have been established, they can be expected to continue beyond the end of a UCDRD-supported project, while the UCDRD program continues to generate new ties between new participants. UCDRD has resulted in first-class collaborative research activities, which involve a significant number of collaborators, postdoctoral fellows, graduate students, and undergraduate students (Fig. 1).

Often, UCDRD funds initiate or strengthen a collaboration by supporting research that takes advantage of existing facilities or of complementary research projects that are funded by other sources such as DOE, the National Science Foundation, or Laboratory-Directed Research and Development. Such synergistic interactions benefit all involved—the scientists, UC campuses, New Mexico universities, Los Alamos, and the agencies supporting the projects.

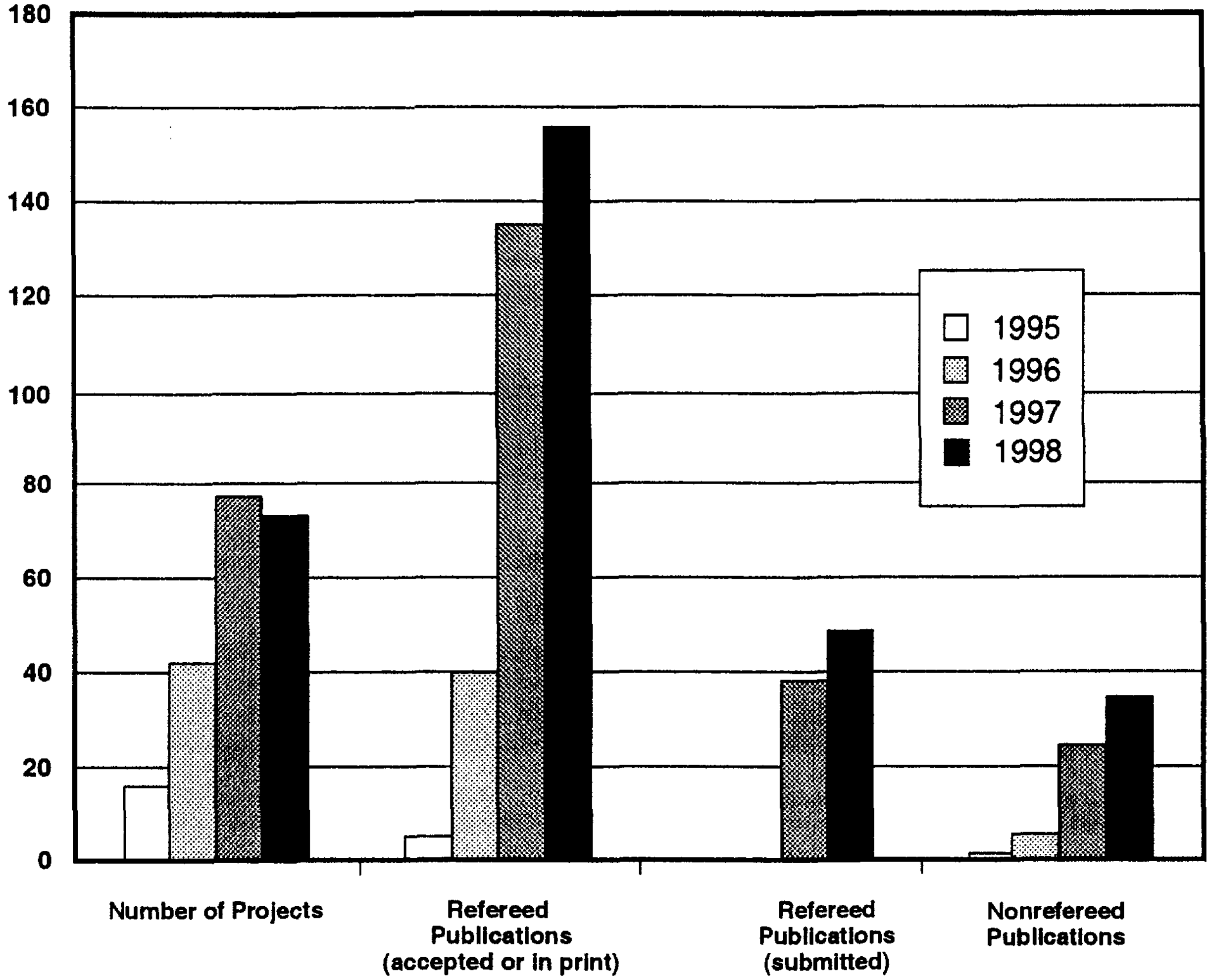


Fig. 2. Number of UCDRD projects and project-related publications for FYs 1995–1998. Publication statistics show separately those research papers accepted for publication or already in print and those submitted (but not yet accepted). The statistics also show those submitted to, accepted by, and printed in the nonrefereed literature (typically conference proceedings). For FYs 1995 and 1996, the statistics included only those publications that were accepted or were in print.

Mutual benefits are evident throughout UCDRD collaborations. The work by university researchers supports selected focus areas that are important to Laboratory core competencies—from biological research and studies of material properties to modeling environmental systems and exploring space. Core competency programs benefit from the influx of university capabilities and fresh ideas; the Laboratory's technical capabilities are increased, along with recruiting opportunities from among outstanding students and postdoctoral researchers. The university researchers get an unparalleled opportunity to interact with the international scientific community. In addition, as their projects bring them to Los Alamos, they become more familiar with the Laboratory's capabilities and facilities such as the Los Alamos Neutron Scattering Center, the advanced free-electron laser, the National High Magnetic Field Laboratory, and Milagro, the high-energy gamma-ray telescope. In addition to broadened training, students enjoy increased possibilities for additional grants and opportunities for employment.

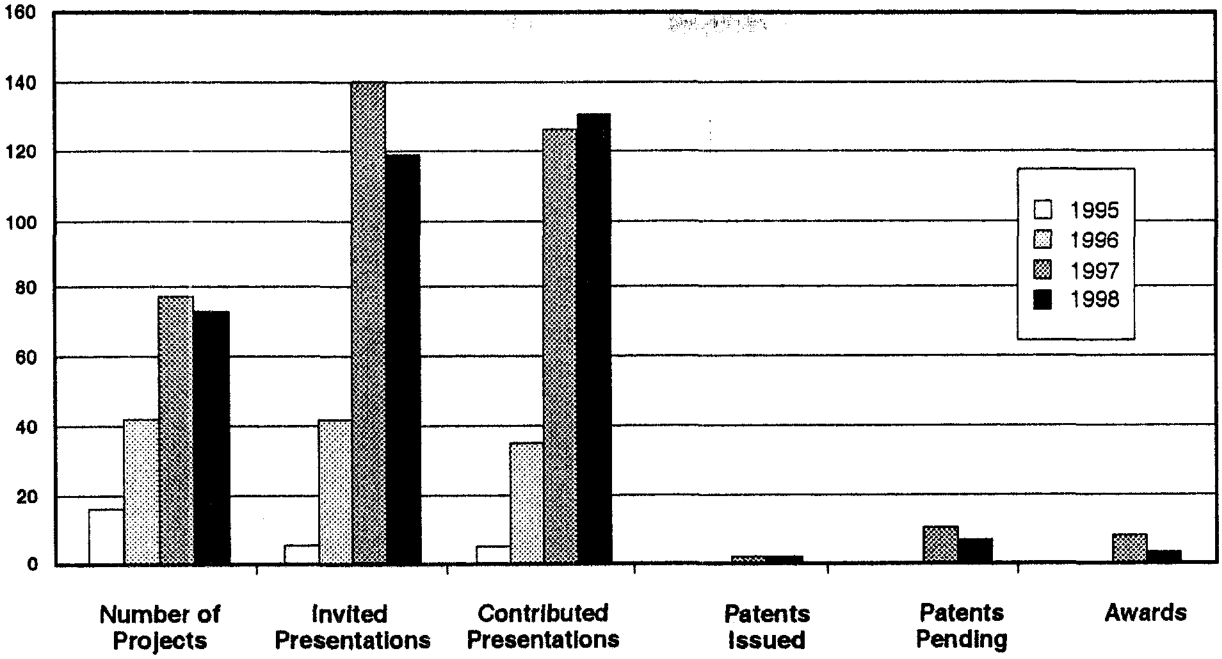


Fig. 3. Number of UCDRD projects and project-related invited and contributed presentations, patents, and awards. Invited presentations are typically seminars, colloquia, and invited talks at technical meetings. Contributed presentations are typically talks or poster presentations given at meetings where these are accepted although not specifically invited.

UCDRD Program Funding. Figure 4 shows the total allocation of UCDRD funds to the CULAR, UCRPI, NUCOR, NMRPI, and Visiting Scholar components for FYs 1995–1998. Actual expenditures in any given fiscal year generally differ from allocations for that year because UCDRD funds do not have to be spent during a given fiscal year; they can be carried over to the next. The progress reports of all individual projects are grouped together for each program component later in the report.

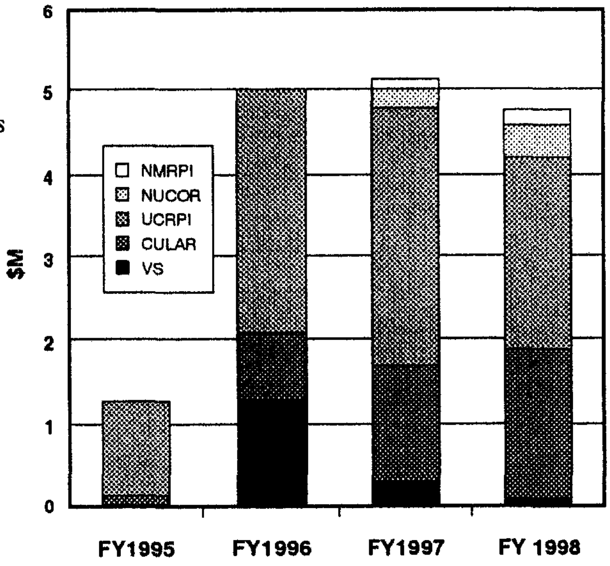
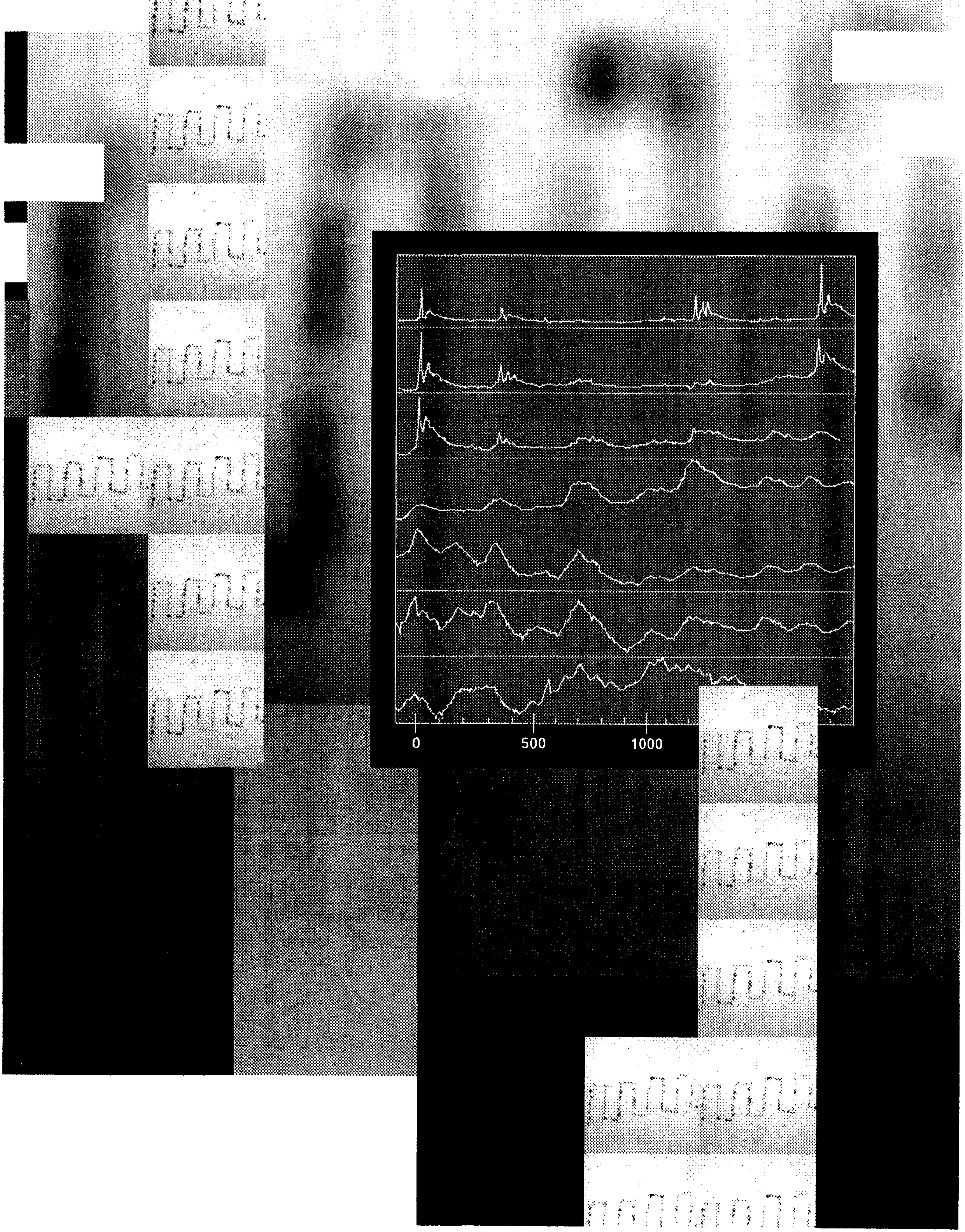


Fig. 4. Allocated funding to CULAR, UCRPI, NUCOR, NMRPI, and Visiting Scholar (VS) program components for FYs 1995–1998.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Collaborative UC/Los Alamos Research (CULAR) Program Progress Reports

The CULAR Program funds joint Los Alamos National Laboratory–UC campus research projects that enhance the Laboratory's competencies in selected areas and, at the same time, strengthen the technical ties between the Laboratory and the UC campuses. Research projects are collaborative in nature and build on the complementary capabilities and research facilities of the Laboratory and the UC campuses involved. A goal of the program is to allow campus participants to become more familiar with Los Alamos capabilities and facilities. The research projects are proposed jointly by Los Alamos and UC campus investigators. Work is performed over a period of up to three years; however, funding is approved for only one year at a time. Depending on the requirements, funding for each project can be as much as $55,000 per year. Most of this funding is spent at the UC campus, but at least $5000 of the funding must be spent at Los Alamos. Each UC campus may submit up to four new proposals to Los Alamos each year, with the research administrator at each campus determining how the proposals are selected at the campus. The proposals undergo peer review by Los Alamos committees for the major technical focus areas. There is a yearly call for CULAR proposals. Additional details of the program are given in the call for CULAR Program proposals, which is available on the World Wide Web at http://stb.lanl.gov/uc.

Thirty-one CULAR proposals were submitted to Los Alamos by the nine UC campuses, and ten new proposals were selected for FY 1998 funding, for a total of thirty-four CULAR projects. These current collaborations are in three focus areas that match the Laboratory's core competencies in bioscience and biotechnology, earth and environmental systems, and materials.

Thirty-three CULAR reports, with listings of personnel, publications, presentations, patents, and awards for FY 1998, follow in this section.

Contents

Final Reports

9802

Nonlinear Optical Response of Linear Polyenes

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Graduate Student: Darcy H. Tarrant, Department of Chemistry, UC Riverside

Abstract

A substantial effort has been devoted to the study of nonlinear optical properties of conjugated polymers, since these materials are promising candidates for optical signal processing devices. However, conjugated polymers are chemically, structurally, and electronically poorly understood. A systematic enhancement and/or tailoring of their nonlinear properties with the goal of device optimization requires a solid experimental and theoretical foundation. Studying the connection between molecular structure and optical response is eased considerably in linear polyenes because of their chemical and structural simplicity. Linear polyenes are well-defined and characterized model systems for conjugated polymers.

The objective of this Collaborative University of California/Los Alamos Research project was to investigate the factors controlling the nonlinear optical response of linear polyenes, both theoretically and experimentally. One of the critical issues determining the optical response in these materials is the position of the even-parity state (m ^1A_g). Key to reliable calculations of nonlinear coefficients is an accurate model for the electronic structure of polyenes. The development of these models is critically dependent on experimental data for the electronic-state properties (like state energies, transition dipole moments, etc.). These data exist only for the 2 ^1A_g state — the locations of higher-lying even-parity states are not known. Moreover, for a comprehensive description of the electronic properties, experimental input data are needed on how changes in chemical, structural, and environmental factors affect ground- and excited-state structure and how these changes in electronic structure affect the structural, electronic, optical, and magnetic responses. Therefore, the experimental aspects of this research project focused on

- locating even-parity states (m ^1A_g with m>2),
- extending the range of experimental data topolyenes with more than four double bonds, and
- investigating the influence of different crystal environments on the electronic states of the polyenes.

The key experimental results of this project are as follows:

- Discovery of at least two new even-parity states of octatetraene. We identified (at least) two new octatetraene electronic states of ^1A_g symmetry, which were labeled 3 ^1A_g and 4 ^1A_g (the third and fourth observable even-parity states).
- Study of interaction mechanisms of polyenes with crystalline environment. A systematic study of the inhomoge-

neous line broadening of the lowest-energy electronic transition of octatetraene in various crystal hosts identified the strain-field-induced geometry changes of octatetraene as the dominant interaction mechanism with the environment.

- Spectroscopic data for longer polyenes. To study how increasing chain length affects the electronic structure, we characterized spectroscopically the two next higher homologues of octatetraene, decapentaene, and dodecahexaene (ground state and first two electronically excited states).

These data serve as solid experimental base data for the models of polyene electronic structure that are concurrently developed at Los Alamos National Laboratory.

Background

One of the principal indices of technological advancement is the speed with which signals can be processed. As carrier frequencies move into the optical domain, the need for new materials that can be used to efficiently and rapidly modify optical frequencies becomes critical. It is now clear that organic molecular materials, particularly those that incorporate unsaturated linear chains (bond-order-wave conjugated materials), are among the most promising candidates for future applications. The main barrier to realizing the potential of these materials is not lack of the ability to make them; organic synthesis has matured to the point where any chemically reasonable structure that can be thought of can be made. The problem is knowing what should be made for optimum applications. Although this may be determined in a completely empirical way, it is far more efficient to proceed from an understanding of the connection between molecular structure and optical response. The present collaboration aims at developing this understanding for the most promising molecular elements, linear polyenes.

Linearly conjugated or bond-order-wave organic materials (polyenes in particular) are paradigm systems for determining how changes in chemical, structural, and environmental factors affect ground- and excited-state structure and how these changes in electronic structure affect the structural, electronic, optical, and magnetic responses. The fact that the p-electrons in linear polyenes are extensively delocalized and highly correlated means that these molecules can have unusually large nonlinear optical responses. Further, since the lowest-energy excited singlet state, the 2 ^1A_g state, is one-photon forbidden but strongly allowed for two-photon absorption, these nonlinear effects can be strongly resonance enhanced at wavelengths well below the one-photon absorption edge. This has already been demonstrated in the case of the disordered and heterogeneous polymer polyacetylene, although the interpretation of the observed resonances is still open to debate. Progress in this area has been slow primarily because the experiments have addressed extremely complicated polymeric materials for which unambiguous structural characterization is lacking.

One of the critical issues controlling optical response in these materials is the position of the even-parity state (m ^1A_g). It is sobering to reflect on the fact that even though the chain length dependence of the excitation energy of the 2 ^1A_g state in linear polyenes has been thoroughly mapped in high-resolution experiments, the location of a higher A_g state has not yet been experimentally established for any polyene.

The experimental aspects of this research project focused on

- locating even-parity states (m ^1A_g with m>2),

- extending the range of experimental data to polyenes with morethan four double bonds, and

- investigating the influence of different crystal environments on the electronic states of the polyenes.

These data serve as solid experimental base data for the models of polyene electronic structure that are concurrently developed at Los Alamos National Laboratory. A second step is calculating the nonlinear optical response from these models. This collaboration is providing the paradigms for designing organic materials with optimized nonlinear optical properties. With this goal we have interactively pursued theory (Los Alamos) and experiment (UC Riverside) to determine the fundamental basis for nonlinear optical response in well-defined model polyenes (unsaturated linear chain conjugated materials). By coupling our theoretical and experimental efforts, we are well on our way to developing the best possible many-body theoretical methods for calculating linear polyene electronic structure and nonlinear optical response. This highly complementary UC Rivrside–Los Alamos collaborative work is laying the foundation for optimizing nonlinear optical response of technologically important low-dimensional electronic materials such as the light-emitting polymers. The highly complementary skills of the two groups are directly contributing to the DOE Los Alamos programs in novel electrooptic materials. The goals of the Collaborative University of California/ Los Alamos Research Program were served extraordinarily well by this research project.

General Principles

Linear polyenes $C_{2n}H_{2n+2}$ (with n being the number of double bonds) belong to the C_{2h} symmetry group in the all-trans configuration, which implies that all p-electron states are of either A_g or B_u symmetry. Since the p-electron system of all linear polyenes contains an even number of electrons, the ground electronic state is always of A_g symmetry (designated in the following as $1\ ^1A_g$ state). The first excited electronic state — the $2\ ^1A_g$ state — has the same symmetry properties as the ground state, which means that the purely electronic 0-0 transition between these states is forbidden for one-photon absorption and fluorescence. Two-photon processes, however, are allowed. One-photon absorption and emission can still be observed when the molecule is in a suitable promoting mode of the ground state. Being of B_u symmetry, the transition from the ground electronic state to second excited electronic state (the $1\ ^1B_u$ state) is one-photon allowed. According to Kacha's rule, irrespective of the initial excitation, fluorescence originates largely from the first excited state — a 0-1 transition into a vibrational mode of the ground state (promoting mode). Obviously, these strictly complementary selection rules are of great value in elucidating the symmetry properties of polyene excited electronic states. For this reason, both one-photon and two-photon spectroscopy were employed to investigate linear polyenes.

Investigating these systems at low temperatures in suitable host matrices, for example, n-alkane crystals, enhances the resolution of the electronic spectra. If the polyenes occupy centrosymmetric sites in the host crystals (like octatetraene in n-octane, decapentaene in n-decane), the selection rules for the polyene electronic transitions remain strictly valid. In a noncentrosymmetric site (like octatetraene in n-hexane) this is no longer true, and the vibrationless $1\ ^1A_g \rightarrow 2\ ^1A_g$ transition becomes weakly one-photon allowed.

Experimental

The excitation source for one-photon fluorescence spectra was a high-pressure xenon lamp filtered through a 0.25-m monochromator (~2-nm bandwidth). The emitted light was collected at right angle, dispersed by a 1.5-m monochromator (spectral resolution 0.2–0.8 cm^{-1}), and detected by a photomultiplier. For one-photon excitation spectra the light from the same high-pressure xenon lamp or from a deuterium lamp was dispersed by the 1.5-m monochromator. Before hitting the sample, a part of the light was split off to serve as a reference. The broad-band fluorescence of the sample was again detected at right angle by a photomultiplier tube. Two-photon excitation spectra were recorded with a N_2 laser-pumped, tunable dye laser. Again, part of the excitation beam was directed to a reference photomultiplier tube. The laser beam was then focused onto the sample and the broad-band fluorescence collected by a photomultiplier tube at right angle. Unless stated otherwise, all experiments were performed at liquid helium temperatures.

Results

The following sections summarize briefly the results of the experimental work in connection with this project. First, the results of the one-photon excitation and fluorescence experiments are presented, followed by the two-photon excitation results. Emphasis is on the discussion of the newly discovered 3 ^1A_g and 4 ^1A_g electronic states of octatetraene. The summary of measured vibrational frequencies in different electronic states focuses on decapentaene, with some data on dodecahexaene. The last paragraph discusses the different interaction mechanisms of linear polyenes with a solid host matrix. It is shown that the bond length distortion of the linear polyenes due to strain fields in the environment is the dominant cause for shifts of the electronic-state energies.

One-Photon Spectra

Octatetraene. The optical spectra of cis- and trans-octatetraene (OT) are well known from previous experiments. The energies of the first two excited electronic states are given in Table 1 for different host materials.

Decapentaene. Decapentaene (n = 5) was synthesized and purified using high-performance liquid chromatography (HPLC). This made it possible to separate cis and trans forms. In general, the spectra are similar to octatetraene.

Of primary interest are the electronic states. Figure 1 shows a one-photon excitation spectrum of trans-decapentaene (DP) in n-heptane. The weakly allowed 1 ^1A_g ’ 2 ^1A_g transition is visible on the low-energy side of the 2 ^1A_g ’ 1 ^1B_u transition. The energies of the first two excited electronic states are given in Table 1 for different host materials.

Dodecahexaene. Dodecahexaene (n = 6) was synthesized in our laboratory. The purification using HPLC provided three fractions, only one of which produced detectable fluorescence. Room-temperature absorption spectra of the three fractions, however, suggest that this fraction contains largely a cis-isomer, whereas one of the other two fractions is largely all trans. However, it is likely that the fraction used in the fluorescence experiments also contains all-trans isomers.

The spectroscopic investigation of dodecahexaene (DDH) proved to be more challenging than the experiments on the shorter polyenes. One reason is that the fluorescence quantum yield decreases rapidly with increasing chain length — the yield for DDH is smaller than the one for OT by two orders of

Sample	$2\,^1A_g$ (cm^{-1})	$1\,^1B_u$ (cm^{-1})	$3\,^1A_g$ (cm^{-1})	$4\,^1A_g$ (cm^{-1})
OT in n-hexane	28,743.9	32,245	45,030	46,880
OT in n-octane	28,565.3	31,949	44,710	46,840
DP in n-heptane	24,724.3	28,802	—	—
DP in n-octane	24,750.1	28,785	—	—
DP in n-decane	24,592	28,575	—	—
DDH in n-decane	21,907.7	26,500	—	—

Table 1. Excited state energies (in cm-1) of the linear polyenes octatetraene (OT), decapentaene (DP), and dodecahexaene (DDH) in various n-alkene host crystals.

magnitude. Furthermore, the solubility of linear polyenes in n-alkanes decreases with increasing length of the polyene chain.

In order for DDH to occupy a substitutional site (and thereby preserving the centrosymmetry), dodecane has to be chosen as host material.
Two complications arise: first, the DDH solubility decreases with increasing length of the host alkane, and second, longer alkane chains are more likely to have twists and dislocation. The latter could prevent the occurrence of the line-narrowing Shpolskii effect.
The highest concentration of DDH was achieved in an n-decane matrix.

The excitation spectrum of the $2\,^1A_g$ state of DDH in n-decane (Fig. 2) shows the 0-0 band and overtones of the double-bond stretch vibration. The energy of the $1\,^1A_g \rightarrow 2\,^1A_g$ transition is given in Table 1.

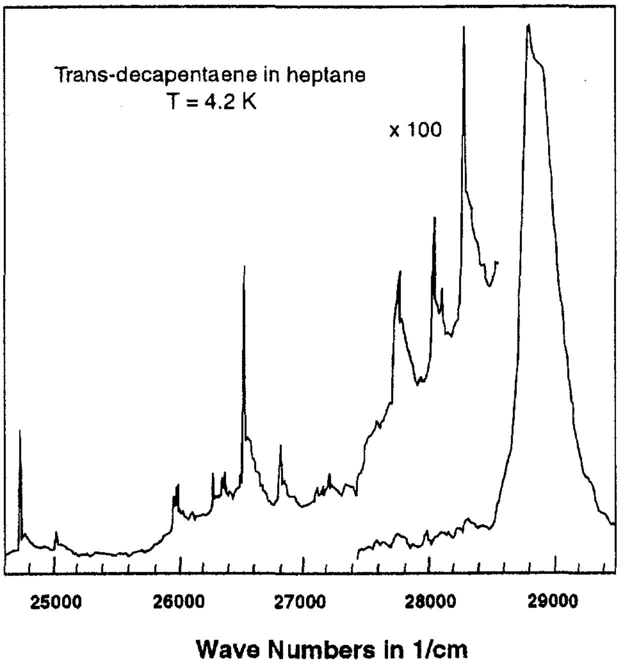


Fig. 1. One-photon excitation spectrum of trans-decapentaene in n-heptane at 4.2 K. The higher sensitivity reveals the weakly allowed $1\,^1A_g \rightarrow 2\,^1A_g$ transition below the $1\,^1A_g \rightarrow 1\,^1B_u$ transition.

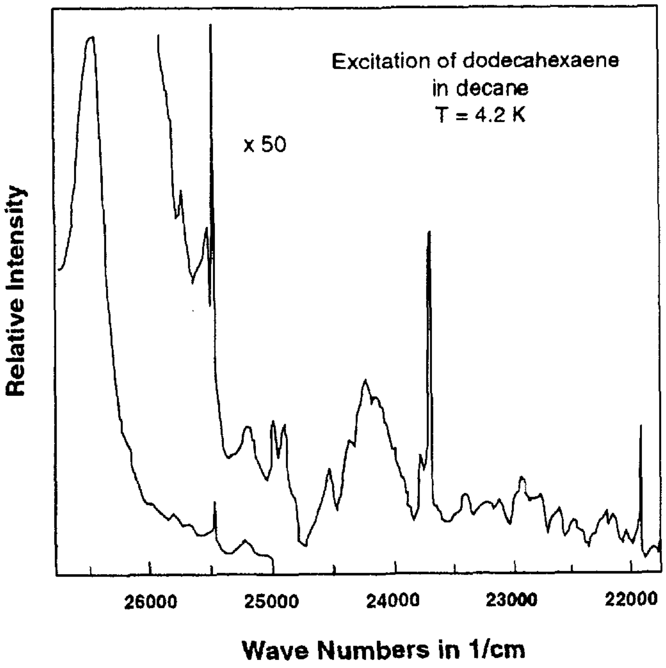
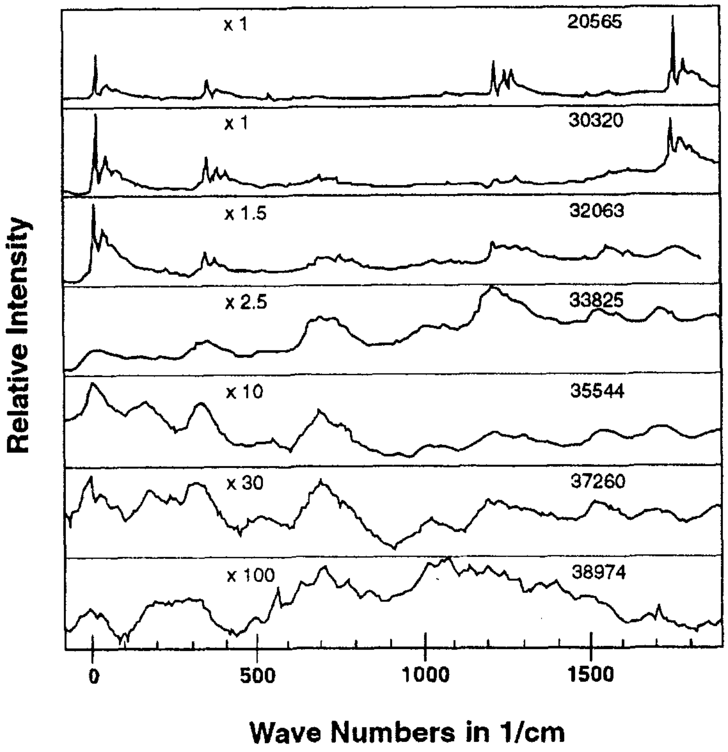


Fig. 2. One-photon excitation spectrum of DDH in decane at 4.2 K. Only the 0-0 1 $^1A_g \rightarrow 2\,^1A_g$ transition and overtones of the C=C double-bond stretch vibration are observed.

Two-Photon Spectra

Octatetraene. In order to locate higher-lying A_g states, two-photon spectra of all-trans octatetraene in n-octane and n-hexane host crystals were recorded in the frequency region between the 1 $^1A_g \rightarrow 2\,^1A_g$ transition energy (which is 28,565 cm^{-1} in n-octane and 28,743 cm^{-1} for n-hexane) and 50,000 cm^{-1}. The latter value is well below the onset of 1 $^1A_g \rightarrow 2\,^1A_g$ one-photon absorption in an n-hexane host. Figure 3 shows the resulting spectrum for the n-octane case up to 40,000 cm^{-1}. The spectrum was divided into segments (Fig. 3), which show immediately that the line pattern is repetitive, showing the vibronic manifold with overtones of the 2 ^1A_g state. Excitation between 40,000 cm^{-1} and 44,000 cm^{-1} did not produce any detectable fluorescence. However, at about 45,000 cm^{-1}, strong fluorescence

Fig. 3. Two-photon excitation spectrum of all-trans octatetraene in n-octane at 1.8 K. The photon excitation energy in cm^{-1} in each panel is given by the number in the upper right corner plus the x-axis value. The upper left corner of each panel shows the intensity magnification factor. The rightmost band in each panel is an overtone of the C=C double-bond stretch fundamental, which is repeated as the first band in the panel below.



again sets in (Fig. 4). In both hosts four bands can be distinguished, which are labeled A–D in Fig. 4. Table 2 lists spectral positions, widths, and intensities relative to the 2 ^1A_g transition. The fluorescence intensity of bands A–D are larger than the fluorescence from the excitation into 2 ^1A_g.

In order to verify the A_g symmetry of these states, one-photon spectra were recorded in the frequency region between 28,000 cm^{-1} and 48,000 cm^{-1}. At low octatetraene concentrations (10^{-5} M) only the one-photon-allowed 1 $^1A_g \rightarrow$ 1 ^1B_u transition was observed. At higher concentrations (10^{-4} M) the weakly allowed 1 $^1A_g \rightarrow$ 2 ^1A_g began to appear. No lines could be detected in the frequency region of the A–D bands, even with concentrations as high as 10^{-3} M. Although given that the intensities of bands A–D after two-photon excitation are larger than 2 ^1A_g excitation, no fluorescence can be detected after one-photon excitation, corroborating the even-parity nature of these bands. Since the C_{2h} symmetry group allows only B_u and A_g states, these states have to be of A_g symmetry.

According to Kacha's rule, we expect that the emitted light following excitation into the bands A–D originates from the 2 ^1A_g state. This means that the fluorescence lifetimes should all be roughly equal, irrespective of the excitation wavelength. Table 2 shows that this is indeed the case.

Another issue has to be addressed: Is it possible that even-parity states exist in the investigated spectral region that — while having significant two-photon cross section — were not observed since they violate Kacha's rule? This implies that there is no efficient decay channel from the m ^1A_g states to the 2 ^1A_g state. Figure 5 depicts possible decay channels for higher-

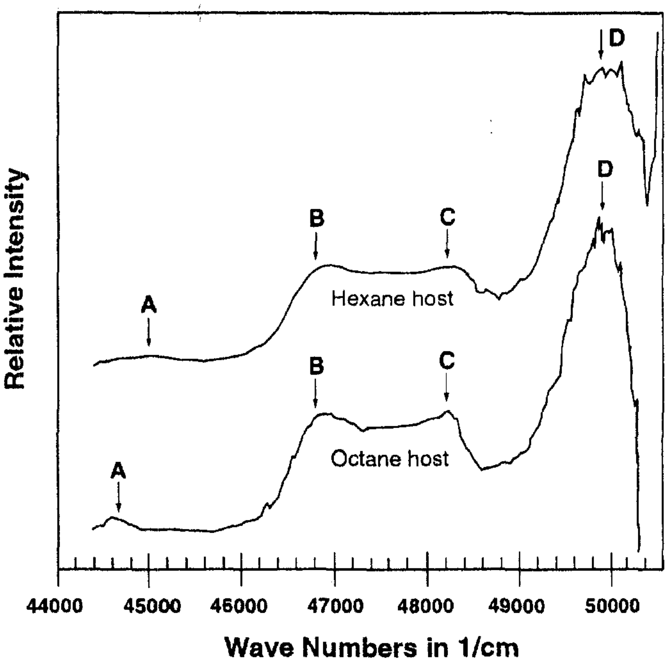


Fig. 4. Two-photon excitation spectrum of the high-energy region of all-trans octatetraene in n-octane at 1.8 K. In each host four bands are observable (labeled A–D).

	Band	Two-Photon Energy (cm^{-1})	FWHM (cm^{-1})	Relative Intensity	Lifetime (ns)
Octatetraene in n-octane	$2\,^1A_g$ 0-0	28,565.3	3.5	1	209
	A	44,710	350	2.3	203
	B	46,840	710	16	216
	C	48,150	1600	20	207
	D	49,830	900	63	185
Octatetraene in n-hexane	$2\,^1A_g$ 0-0	28,743.9	4.0	1.7	90
	A	45,030	460	2.6	90
	B	46,880	900	17	91
	C	48,070	1300	21	97
	D	49,900	1040	64	88

Table 2. Energies, widths (FWHM, or full widths at half maximum), relative intensities, and fluorescence lifetimes of bands A-D compared with the respective values for the $2\,^1A_g$ state. The relative intensities are calculated with respect to the intensity of the $1\,^1A_g \rightarrow 2\,^1A_g$ transition of octatetraene in n-octane.

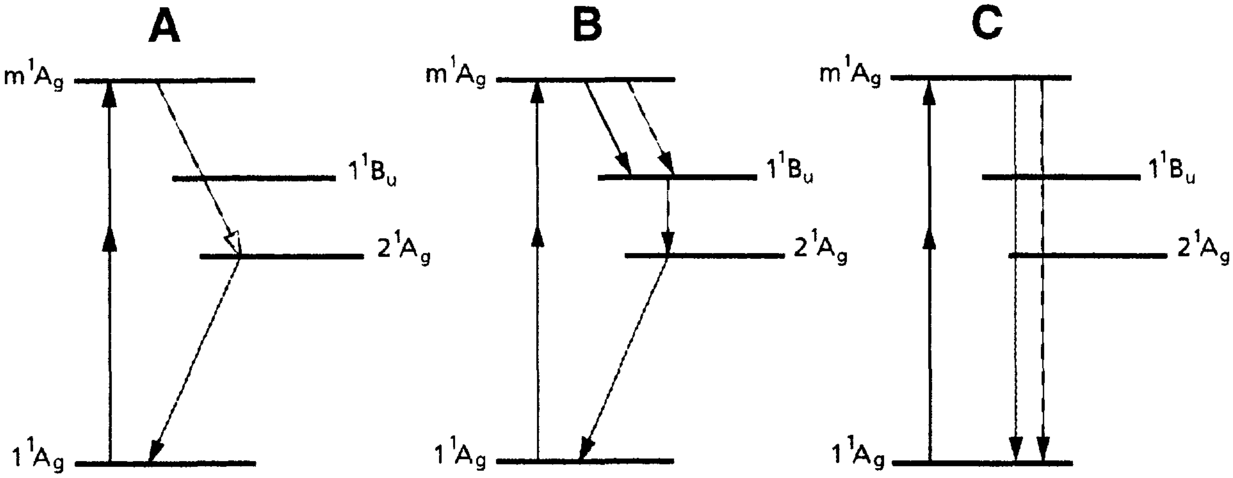


Fig. 5. Singlet manifold decay channels for higher-lying ^1A_g states. Solid lines indicate two-photon excitation, dotted lines denote radiative decay, and dashed lines represent nonradiative relaxation.

lying A_g states. Octatetraene in an m ^1A_g state can dispose of its energy by

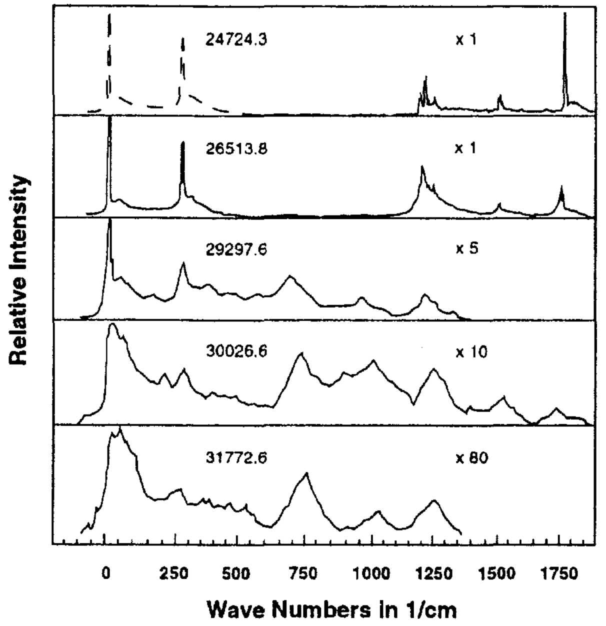
- radiative or nonradiative decay into the 1 ^1B_u state (including its vibronic manifold) (process A),
- radiative or nonradiative decay into the 1 ^1B_u state (including its vibronic manifold) (process A), and
- radiative or nonradiative decay into the 1 ^1A_g ground state (including its vibronic manifold) (process C).

From earlier experiments it is known that direct excitation into the vibronic manifold of the 2 ^1A_g and 1 ^1B_u states results in fluorescence from the 2 ^1A_g state. Therefore, processes A and B will also result in fluorescence from the 2 ^1A_g state. Thus, a higher-lying A_g state would only be missed if it directly converted into the vibronic manifold of the ground state (process C). A direct radiative transition from an m ^1A_g state to the ground state is symmetry forbidden, which strongly favors decay into the 1 ^1B_u state (which in turn leads to normal fluorescence). This leaves the ultrafast radiationless decay into the vibronic manifold of the 1 ^1A_g state to be considered. The energy released in this process will either create lattice phonons or highly excited ground-state vibrations. The probability for these processes decreases with increasing energy because of an increasing energy mismatch and smaller vibrational overlap. Moreover, one expects this type of radiationless decay to be faster from the vibrationally excited levels of the 2 ^1A_g state than from the higher-lying ^1A_g states. It is known, however, that the former leads to normal fluorescence, which shows that the direct radiationless decay rate in not high enough to compete with the normal fluorescence. In summary, all these considerations lead to the conclusion that excitation into higher-lying ^1A_g states will result in fluorescence from the 2 ^1A_g state. Therefore, there are no additional ^1A_g states in the spectral region between 28,000 cm^{-1} and 50,000 cm^{-1} with observable two-photon cross sections.

Now we can proceed to assign the bands A–D to vibronic states. Band A is assigned to a new 3 ^1A_g state ("3" means the third observable ^1A_g state). This assignment is based on the 300 cm^{-1} difference of the solvent shift in n-hexane and n-octane. Since this difference is only 179 cm^{-1} for the 2 ^1A_g state, band A has to be a new origin band. Bands B–D could be vibronic additions to the 3 ^1A_g state; however, the different solvent shifts going from n-hexane to n-octane seem to rule out this possibility. Therefore, band B is assigned to a new 4 ^1A_g state. With the available data it is not possible to decide whether bands C and D are vibronic additions to the 4 ^1A_g state or new ^1A_g states.

In summary, the available data lead to the identification of (at least) two new octatetraene electronic states of ^1A_g symmetry. It has to be reemphasized that these states, which were labeled 3 ^1A_g and 4 ^1A_g, are the third and fourth observable even-parity states. It cannot be excluded that the investigated spectral region contains further A_g states with an unobservably small two-photon cross section.

Decapentaene. Figure 6 shows a fluorescence excitation spectrum of trans-decapentaene in n-heptane. Again, as in Fig. 3, in order to emphasize the repetitive nature of the spectrum, it was divided into segments, which were plotted stacked. The 0-0 band of the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition lies in the region of 24,450 cm^{-1} and 24,750 cm^{-1} depending on the host material. The output of the utilized laser system for two-photon absorption into this band was insufficient. For this reason, the 0-0 band is missing in Fig. 6. The position of this band can, however, be calculated from the observed five overtones of the C=C double-bond stretch vibration. The result is shown in Fig. 7, which compares the one-photon and two-photon



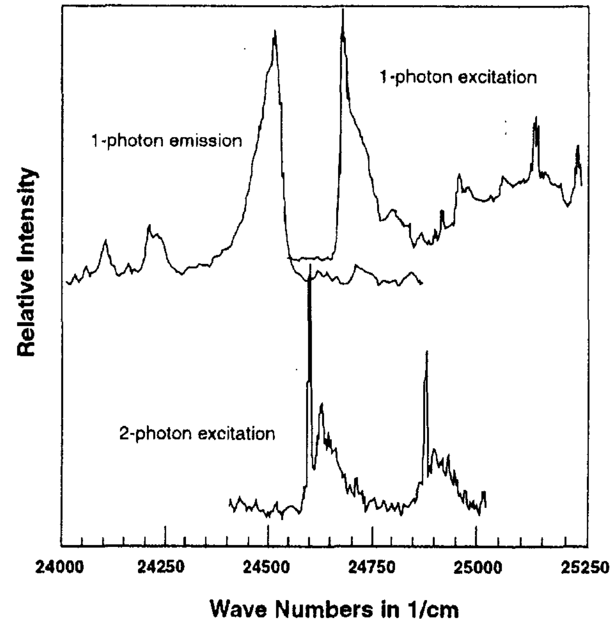


Fig. 6. Two-photon excitation spectrum of trans-decapentaene in n-heptane at 1.8 K. The rightmost band in each pane is an overtone a C=C double-bond stretch vibration. This line is repeated at the left edge of the panel below. The photon excitation energy in cm^{-1} *in each panel is given by the number in the upper right corner plus the x-axis value. The upper left corner of each panel shows the intensity magnification factor.*

Fig. 7. The 0-0 band of the $1\,{}^1A_g \rightarrow 2\,{}^1A_g$ *transition of trans-decapentaene in decane measured by one-photon excitation, one-photon fluorescence and two-photon excitation. The two-photon spectrum was extrapolated from overtones (see text). The one-photon transition occurs via a low-frequency vibrational mode (promoting mode) of* b_u *symmetry.*

spectra of the 0-0 band of the $1\,{}^1A_g \rightarrow 2\,{}^1A_g$ transition of trans-decapentaene in n-decane. These spectra demonstrate that the selection rules are still strictly valid, implying that trans-decapentaene occupies a centrosymmetric site in n-decane. The energies of the two lowest excited electronic states in different hosts are listed in Table 1. It was not possible to detect any fluorescence after two-photon excitation with energies above 35,000 cm^{-1}.

Dodecahexaene. Because of insufficient concentration and a very low fluorescence quantum yield, it was not possible to measure two-photon excitation spectra for DDH.

Summary: Linear Polyene Electronic States

Table 1 summarizes the energies of the hitherto measured excited electronic states of trans-OT, trans-DP, and DDH in various n-alkane hosts. This table was compiled by combining the results from one-photon excitation and emission spectra and from two-photon excitation spectra.

Summary: Vibrational Frequencies

Trans-Species. Tables 3–5 summarize the vibrational frequencies of trans-octatetraene (OT) and trans-decapentaene (DP) in various n-alkanes for the $1\ ^1A_g \rightarrow 2\ ^1A_g$, and $1\ ^1B_u$ states. Earlier data of octatetraene are included in order to facilitate comparison with the new decapentaene results.

Cis-Species. Since cis-isomers of linear polyenes do not possess C_{2h} symmetry, the symmetry labels that were used for the trans-species are no longer valid. They are used Tables 6 and 7 to label excited electronic states of the cis-polyenes.

$1\ ^1A_g$	Single Bond 1 (cm^{-1})	Single Bond 2 (cm^{-1})	Single Bond 3 (cm^{-1})	Single Bond 4 (cm^{-1})	Double Bond 1 (cm^{-1})	Double Bond 2 (cm^{-1})
OT/octane	1183	1286	—	—	1607	—
DP/heptane	1130.9	1180.9	1296.8	—	1603.5	—
DP/octane	1129.9	1180.0	1295.1	—	1600.3	—
DP/decane	1126.1	1173.7	1290.7	—	1588.2	—

Table 3. Vibrational frequencies in the $1\ ^1A_g$ state of trans-octatetraene (OT) and trans-decapentaene (DP) in various n-alkanes measured at liquid helium temperatures.

$2\ ^1A_g$	Single Bond 1 (cm^{-1})	Single Bond 2 (cm^{-1})	Single Bond 3 (cm^{-1})	Single Bond 4 (cm^{-1})	Double Bond 1 (cm^{-1})	Double Bond 2 (cm^{-1})
OT/octane	1218	1272	—	—	1753	—
DP/heptane	1221.4	1247.1	1278.2	—	1532.1	1798.2
DP/octane	1221.3	1249.3	1278.1	—	1531.2	1797.0
DP/decane	1224	—	—	—	1518.4	1783.0

Table 4. Vibrational frequencies in the $2\ ^1A_g$ state of trans-octatetraene (OT) and trans-decapentaene (DP) in various n-alkanes measured at liquid helium temperatures.

$1\,^1B_u$	Single Bond 1 (cm^{-1})	Single Bond 2 (cm^{-1})	Single Bond 3 (cm^{-1})	Single Bond 4 (cm^{-1})	Double Bond 1 (cm^{-1})	Double Bond 2 (cm^{-1})
OT/octane	—	—	—	—	—	—
DP/heptane	1246	—	—	—	1686	—
DP/octane	1208	—	—	—	1628	—
DP/decane	1237	—	—	—	—	—

Table 5. Vibrational frequencies in the $1\,^1B_u$ state of trans-octatetraene (OT) and trans-decapentaene (DP) in various n-alkanes measured at liquid helium temperatures.

$1\,^1A_g$	Single Bond 1 (cm^{-1})	Single Bond 2 (cm^{-1})	Single Bond 3 (cm^{-1})	Single Bond 4 (cm^{-1})	Double Bond 1 (cm^{-1})	Double Bond 2 (cm^{-1})
OT/octane	1187	1286	—	—	1606	—
DP/heptane (site 1)	1157.4	1383.1	—	—	—	1610.9[a]
DP/heptane (site 2)	1155.3	1183.5	—	1247.5	—	1607.1[a]
DP/octane	1154.7	1181.5	1224.9	1249.4	1493.3[b]	1598.6[a]
DP/decane	1150.8	1179.2	1223.9	1255.3	1486.1[b]	1589.7[a]
DDH/decane	1135.8	1176.5	1232	1239.7	2579.2	—

[a] $C_3{=}C_4$ double-bond vibration.

[b] Double-bond totally symmetric vibrational stretch modes.

Table 6. Vibrational frequencies in the $1\,^1A_g$ state of cis-octatetraene (OT), cis-decapentaene (DP), and cis-dodecahexaene (DDH) in various n-alkanes measured at liquid helium temperatures. Cis-decapentaene occupies two sites in n-heptane with roughly equal probabilities.

$2\,^1A_g$	Single Bond 1 (cm^{-1})	Single Bond 2 (cm^{-1})	Single Bond 3 (cm^{-1})	Single Bond 4 (cm^{-1})	Double Bond 1 (cm^{-1})	Double Bond 2 (cm^{-1})
OT/octane	—	—	—	—	—	—
DP/heptane (site 1)	1154.2	1213.4	1295.4	1323.3	1531.2	1778.6
DP/heptane (site 2)	1156.8	1211.5	—	1325.1	1533.3	1777.2
DP/octane	1140.2	1212.3	1298.3	1325.6	1529.2	1774.1
DP/decane	1128.3	1211.1	—	1313.3	1522	1771.7
DDH/decane	—	—	—	—	1520	1784.1

Table 7. Vibrational frequencies in the 2 ^1A_g state of trans-octatetraene (OT), trans-decapentaene (DP), and trans-dodecahexaene (DDH) in various n-alkanes measured at liquid helium temperatures. Cis-decapentaene occupies two sites in n-heptane with roughly equal probabilities.

Guest-Host Interaction Mechanisms

Inhomogeneous broadening of electronic absorption lines is ubiquitous in molecular guest-host systems. For example, the ratio of inhomogeneous to homogeneous line width of the $1\,^1A_g \rightarrow 2\,^1A_g$ of octatetraene in n-hexane is about 30,000. It is known that the basic reason for inhomogeneous line broadening is that because of strain fields, dislocations, etc., the guest molecules do not have identical local environments. This distribution of local environments leads to a distribution of transition energies, since the guest-host interaction depends on the local structure.

In order to arrive at a microscopic picture of inhomogeneous line broadening, the local structure around the guest molecule be known. So far, no detailed microscopic picture exists, since it has not been possible to determine the distribution of local environments at a microscopic level (that is the position of all atoms within the interaction range of the guest molecule).

To have a well-defined experimental situation, where changes to the local structure can be linked to the broadening of the line, we investigated octatetraene doped n-octane and n-hexane crystals, with n-alkane molecules replaced by matching halogenated alkanes in increasing concentrations. These (in effect) "atomic" substitutions cause additional inhomogeneous broadening, because they modify each of the following three guest host interaction mechanisms:

- The guest molecule is subjected to a strong electric field (the internal electric field), which is generated by the charge distributions on the surrounding host molecules.

- Especially in the case of a nonmatching substitution (i.e., octatetraene in n-hexane as compared with octatetraene in n-octane), the strain fields generated will change the octatetraene geometry slightly (i.e., bond lengths, bond angles).

- A further contribution to the solvent-shift is due to the dispersive interaction (fluctuating charge distributions).

Replacing a hydrogen atom with a halogen has the following consequences:

- the n-alkane charge distribution is altered, which changes the strength of the electrostatic interaction;

- the n-alkane polarizability is modified, which influences the dispersive interaction; and

- the larger size of the halogens creates additional strain fields, which in turn will modify the octatetraene geometry.

These effects lead to additional line shifts. The statistical aspects of inhomogeneous broadening enter by considering all possible locations of the halogen atom with respect to octatetraene. The inhomogeneous line shapes were measured depending on the concentration of halogenated alkanes. The perturbed inhomogeneous lines can be described as a convolution of the original inhomogeneous line shape (without halogenated alkanes in the sample) with some function that describes the additional broadening caused by the halogenated alkanes. In our case, the additional broadening function is best described by a Lorentzian. In all cases, the width of this Lorentzian increases linearly with the concentration of halogenated alkanes. Analyzing the contributions to this Lorentzian yields information about the dominant guest-host interaction mechanisms. The basis for all calculations is exact knowledge — at a microscopic level — of the local environment of the guest molecule. That is, we need to know the positions of all atoms making up guest and host molecules. This was accomplished with molecular mechanics simulations. For each possible position of the halogen atom with respect to octatetraene, the minimum energy structure was determined. This provided — for the first time — a microscopic distribution of local environments. Given the exact geometry, the additional inhomogeneous broadening can be calculated for each of the different interaction mechanisms separately and compared with the experimental data.

The results show that the main reason for additional inhomogeneous broadening in the investigated systems is the fluctuation of single and double carbon-carbon bond lengths of octatetraene resulting from variations in the local environment. Although the relative fluctuations of intramolecular distances (10^{-4}) are much smaller than intermolecular ones (10^{-3}), the extreme sensitivity of the guest molecule transition energies to bond length changes causes the former to have a much larger effect on the transition energies.

This shows that strain fields are most effective in changing the transition energies of linear polyenes. The fact that slight distortions of molecules can have drastic effects on molecular spectra is also seen in the transition dipole moments. The "0-0" $1\ {}^1A_g \rightarrow 2\ {}^1A_g$ transition of octatetraene in n-octane is strictly symmetry forbidden, while the "0-1" $1\ {}^1A_g \rightarrow 2\ {}^1A_g$ transition in the same system can be quite intense if the vibrational mode is of b_u symmetry.

Refereed Publications

Geissinger, P., B.E. Kohler, S.G. Kulikov, and V. Terpougov, "Inhomogeneous Broadening of Electronic Spectra in Organic Model Systems," *J. Chem. Phys.* **108**, 1821 (1998).

Kohler, B.E., and V. Terpougov, "Electronic States of Linear Polyenes: High Resolution Spectroscopy of Cis-and Trans-1,3,5,7,9-Decapentaene," *J. Chem. Phys.* **108**, 9586 (1997).

Kohler, B.E., and V. Terpougov, "Two-Photon Excitation Spectra of Higher Lying m ^1A_g States of Octatetraene," *Synth. Met.* 84, 927 (1997).

Kohler, B.E., and J.C. Woehl, "Conjugation Lengths in Long Polyene Chains," *Synth. Met.* **84**, 851 (1997).

Kohler, B.E., and J.C. Woehl, "Effects of Internal Electric Fields and Electrostatic Potentials on Optical Spectra of Linear Polyenes," *Synth. Met.* **84**, 859 (1997).

Presentations

Geissinger, P. "Die Inhomogene Verbreiterung in Organischen Mischkristallen (Inhomogeneous Broadening in Organic Mixed Crystals)," Department of Experimental Physics IV Seminar, University of Bayreuth, Bayreuth, Germany, September 10, 1997 (invited).

Geissinger, P., B.E. Kohler, S.G. Kulikov, and V. Terpougov, "A Microscopic Model of the Inhomogeneous Broadening of Electronic Transitions in Solid Guest/Host Systems," Meeting of the American Physical Society, Los Angeles, CA, March 16–20, 1998.

Geissinger, P., B.E. Kohler, S.G Kulikov, and V. Terpougov, "Inhomogeneous Broadening of Electronic Transitions in Mixed Crystals," 45th Annual Meeting, Western Spectroscopy Association, Pacific Grove, CA, January 28–30, 1998.

Geissinger, P., B.E. Kohler, S.G. Kulikov, and V. Terpougov, "Inhomogeneous Broadening in Organic Model Systems," Western Regional Meeting of the American Chemical Society, Irvine, CA, October 21–25, 1997 (contributed).

Geissinger, P., B.E. Kohler, S.G. Kulikov, and V. Terpougov, "Inhomogeneous Broadening in Organic Model Systems," Gordon Research Conference on Molecular Electronic Spectroscopy and Dynamics, Oxford, United Kingdom, August 31–September 5, 1997 (contributed).

Kohler, B.E., and V. Terpougov, "High Resolution Spectra of Cis- and Trans-Decapentaene," 44th Annual Meeting, Western Spectroscopy Association, Pacific Grove, CA, January 29–31, 1997 (contributed).

Kohler, B.E., S.G. Kulikov, and V. Terpougov, "Inhomogeneous Broadening in Organic Model Systems," 44th Annual Meeting, Western Spectroscopy Association, Pacific Grove, CA, January 29–31, 1997 (contributed).

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Structure and Interactions in Nucleic Acid-Membrane Systems: Bioengineering Strategies for the Development of Nonviral Vectors

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Abstract

The project objective was to elucidate the mechanisms by which cationic-liposome-based nonviral vectors facilitate the uptake of nucleic acids and peptides (models of therapeutic drugs) by mammalian cells. The long-range ultimate goal is to develop efficient synthetic carriers of DNA and peptides for gene and drug therapy and disease control. There is now a surge of activity in developing synthetic nonviral carriers (vectors) of DNA and peptides for gene therapy and, more generally, drug therapy applications, because of their low toxicity, nonimmunogenicity, and ease of production. In particular, cationic-liposome-DNA (CL-DNA) complexes have shown gene expression in vivo in targeted organs, and human clinical protocols are ongoing. However, because the mechanism of action of CL-DNA complexes remains largely unknown, transfection efficiencies are at present very low and vary by up to a factor of 100 in different cell lines. This unpredictability is attributable to a lack of knowledge regarding the structures of CL-DNA and CL-peptide complexes and their interactions with mammalian cells. We combined x-ray and neutron small-angle scattering with light microscopy in our studies of the structures of CL-DNA (with reporter genes) and CL-peptide complexes. The studies have lead to the important finding that CL-DNA and CL-peptide complexes self-assemble into lamellar and hexagonal structures with controllable DNA or peptide drug-carrying capacity.

Background

Introduction. Gene and drug therapy depend on the successful transfer and expression of extracellular DNA to the nucleus of eucaryotic cells, with the aim of replacing a defective gene or adding a missing gene.[1] Viral-based carriers of DNA are currently the most common method of gene delivery, but there has been a tremendous activity in developing synthetic nonviral carrier.[2] In particular, cationic liposomes (CLs),[3] in which the overall positive charge of the cationic-liposome-DNA (CL-DNA) complex enhances transfection by attaching to anionic animal cells, have shown gene expression in vivo in targeted organs,[4] and human clinical protocols are ongoing.[5] CL transfer vectors exhibit low toxicity, nonimmunogenicity, and ease of production, but their mechanism of action remains largely unknown with transfection efficiencies varying by up to a factor of 100 in different cell lines.[2-6] This unpredictability, which is ubiquitous in gene therapy[7] and in particular in synthetic systems (the focus of our research), may be attributed to a lack of knowledge regarding the interactions between CL-DNA complexes and animal cells; in particular, the mechanisms involved in the route of cell entry, the transfer to the nuclear region, and the delivery of DNA within the nucleus remain unknown.

Research Objectives. Our research uses a variety of x-ray scattering and light microscope-based direct-imaging techniques[8,9] combined with recombinant DNA methodologies[10] (in preparing specific DNA constructs with the appropriate promoter and reporter gene for the quantitative monitoring of transfection) and synthesis of different chemical carriers.[11] With these tools we plan to elucidate (a) the mechanisms by which CL-based nonviral vectors facilitate the uptake of nucleic acids by mammalian cells, (b) the spatial and temporal distribution of the CL-DNA complex in the cytoplasm to elucidate the mechanism or mechanisms of transport of the complex to and across the nucleus, and (c) the transfection rates by monitoring gene expression. Modeling[12] of DNA-cationic lipid systems should guide us in optimizing some of the key experimental parameters, such as the liposome charge density, optimal liposome size, and ratios of lipid to nucleic acid. The ultimate goal of the project is to use the knowledge gained in the design and synthesis of optimal nonviral transfection reagents. For these purposes, we have designed a series of experiments centered around unraveling the interactions and resulting structures in mixtures of nucleic acid and lipid. Both very simple model systems and animal cell lines will be used in these experiments.

Importance to Los Alamos Science and Technology Base and National Research and Development Needs. The most immediate biotechnological ramifications of the research is in the area of drug therapeutics and gene therapy. However, the research should also shed light on other problems in biology that very often lead to important applications in biotechnology. These include (a) DNA interactions with nuclear membrane during replication; (b) the biology of transport of antisense RNA across membranes used by plant, animal, and microbial cells to control gene expression, and the mechanism of transport of DNA across nuclear membrane in triplex DNA formation; (c) plasmid DNA transfer between conjugating bacteria; and (d) the biology of trafficking between plasma membrane and nuclear membrane of endosome and lysosome organelles associated with microtubules relevant to transport of DNA complexes incorporated within these organelles. The successful proposal would lead to the development of optimal nonviral carriers of DNA vectors in gene therapy. In addition, the success of the proposal will also have implications in the area of efficient delivery of antisense-RNA. Antisense-RNA and triplex-DNA are short oligonucleotide gene regulatory molecules currently explored by biotech companies for their use in gene therapeutics.

Scientific Approach (Capabilities at the Campus and Los Alamos). Synchrotron x-ray scattering (UC Santa Barbara and Los Alamos joint facility) experiments are carried out at the Stanford Synchrotron Radiation Laboratory, which is a national facility supported by the Department of Energy (DOE). In addition, three of our researchers are partners in the Complex Materials Consortium (Princeton, UC Santa Barbara, University of Pennsylvania, University of Tennessee, Los Alamos, Oak Ridge National Laboratory, Exxon, and Brookhaven National Laboratory), which is building a beam line at the upcoming APS at Argonne National Laboratory with support from DOE and the National Science Foundation.

The SPEAR reflectometer at the Los Alamos Neutron Science Center (LANSCE) is a world-class instrument for measuring neutron reflectivity (e.g., at the DNA/lipid interface). The small-angle capabilities at LANSCE are also exceptional. In addition, an x-ray diffraction facility with one rotating-anode generator is available at LANSCE. Los Alamos has set up a variety of thin-film deposition techniques, in particular, the

Langmuir-Blodgett trough and the film-spinning facility, which can be used to prepare multilayer membrane samples.

The College of Engineering at UC Santa Barbara has imaging capabilities to be used in this project; they include video-enhanced light microscopy techniques of phase, differential interference, and reflection interference contrast, together with fluorescence microscopy. Also included are micropipette capabilities and cell-culturing facilities. In addition, the Materials Research Laboratory at UC Santa Barbara, a multidisciplinary research center funded by the National Science Foundation, supports user facilities in x-ray scattering that house a number of state-of-the-art instruments for x-ray diffraction, including two 18-kW Rigaku rotating-anode generators and two small-angle scattering diffractometers.

Progress

Synchrotron X-Ray Scattering of DNA-Cationic Membrane Condensates. Our recent work using differential interference contrast, fluorescence light microscopy, and x-ray diffraction has revealed distinct states of the CL-DNA complexes in water.[9] These data show that the structure is significantly different from the previously hypothesized bead-on-string structure. Figure 1 shows small-angle synchrotron x-ray data of an extremely dilute DNA-cationic liposome mixture in water ($\approx$ 99% water) for positive CL-DNA complexes with lipid-to-DNA (L/D) ratio $L/D = 6$ (wt/wt). (Stoichiometric charge neutrality occurs around $L/D \approx 4.4$ (wt/wt). The complexes form globular condensates. Unexpectedly, the x-ray data of the complexes reveal a layered structure for the lipid membrane. This is seen by the presence of the two narrow peaks (at $q = 0.096$ Å^{-1} and 0.192 Å^{-1}), which correspond to the (00L) peaks of a layered structure with an interlayer spacing $d = 65.4$ Å.

The middle broad peak arises from DNA-DNA correlations and gives an average DNA-DNA distance of 48 Å. (The intra-DNA peak occurs at much larger q.) In the absence of DNA, the multilamellar L_α phase of this charged lipid-water mixture gives rise to very large interlayer spacings of order 1000 Å (at 99% water) due to long range electrostatic interactions. The DNA that appears to condense on the cationic lipid layer strongly screens this interaction, leading to a collapse of bilayers into condensed multilayers. The individual globules (i.e., similar to what is shown in Fig. 2) thus consist of (finite-sized) lipid multilamellar structures with DNA sandwiched between the bilayers. The interlayer spacing of $d = 65.4$ Å is consistent with this picture, since the lipid bilayer has been measured to have a thickness of 40 Å, and DNA has a diameter of 25 Å (in the common B form). Understanding the variables that control the packing of DNA between bilayers will undoubtedly be correlated with the transfection efficiency.

Neutron and X-Ray Scattering of Cationic Liposome-Polypeptide Complexes. Complexes of cationic lipids with negatively charged biological polyelectrolytes such as DNA and proteins have elicited much interest recently because of their potential applications in gene therapy and in developing novel biomolecular materials. We have investigated the structure of complexes made from the anionic polypeptide poly-L-glutamic acid (PGA) and a positively charged lipid mixture consisting of the cationic lipid didodecyl dimethyl ammonium bromide (DDAB) and the neutral lipid dilauroyl-sn-glycero phosphocholine (DLPC).[13] Small-angle x-ray and small-angle neutron scattering and optical microscopy of the complexes are consistent with a condensed multilamellar structure with PGA molecules sandwiched between the bilayers of the lipids (Fig. 2). Moreover, the data indicate that the PGA molecules do not exhibit any kind of orientational or positional correlations on the plane of the bilayers.

Lipid dilution experiments were carried out by systematically increasing the ratio of the neutral lipid to the cationic lipid but still maintaining the stoichiometric balance between the cationic lipid and PGA. These experiments revealed that the complexes remained stable even at very high lipid dilutions (high fraction of neutral lipid in the membrane) and that the interlamellar *d*-spacing increases monotonically from 39 Å for the pure DDAB membrane to 60 Å at very high dilutions. While lipid chain stretching alone does not account for the increase in *d*-spacing, we propose a "pinching" mechanism, where at high lipid dilutions the PGA molecules and DDAB molecules are localized to form a tightly packed layer (pinch). Away from these pinches the system behaves as pure DLPC membrane with an equilibrium spacing of 60 Å. The morphology of the complexes is unchanged when the molecular weight and the monodispersity of the PGA are increased.

It has been realized in recent years that ordered microstructures formed through a noncovalent self-assembly process lead to materials with unusual optical, electrical, mechanical, and biological properties. Polyelectrolyte-surfactant complexes represent a class of ordered microstructured materials exhibiting a rich variety of phase morphology. These complexes are formed by spontaneous self-assembly of the surfactants with oppositely charged polyelectrolytes in aqueous solutions. The driving forces for the formation of such complexes are from the usual hydrophobic-hydrophilic balance of the surfactants combined with a strong electrostatic interaction between the charged components. Since the self-assembly process is noncovalent, the macroscopic properties of the complexes can be suitably tailored by varying the molecular interactions of the self-assembly

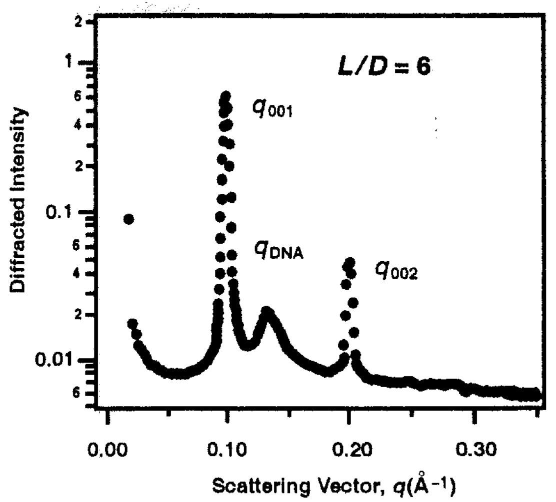

Fig. 1. Synchrotron x-ray scattering data on a dispersion of cationic liposome-DNA complexes in water. The peaks reveal a multilamellar structure with DNA sandwiched between bilayers shown schematically in Fig. 2. The broad peak in the middle is due to the DNA-DNA correlations [from Ref. 9: Science *275, 810 (1997)].*

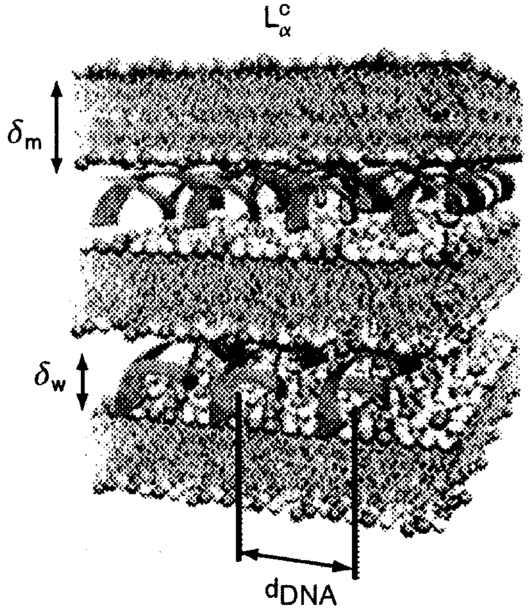

Fig. 2. Schematic of the lamellar L_α^C phase of cationic liposome-DNA complexes with alternating lipid bilayer and DNA monolayer. The DNA interaxial spacing is d_{DNA}. *The interlayer spacing is* $d = \delta_w + \delta_m$ *[from Ref. 9:* Science *275, 810 (1997)]. The cationic liposome-peptide complexes form a similar lamellar structure, however, with the peptide sandwiched between bilayers in a disordered array.*[13]

process by changing temperature, solvent conditions, and surfactant charge, for example. The understanding that the study of these systems can bring to the problem of self-assembly and the wide array of surfactants and polyelectrolytes available have elicited considerable interest in this area. The various phase morphologies of polyelectrolyte-surfactant complexes make them promising materials for (a) template-directed synthesis of inorganic zeolites, (b) layer-by-layer creation of organic thin films, (c) novel biomolecular materials, and, most important, (d) gene therapy.

To date, work in this area has mainly focused on the complexation between synthetic polyelectrolytes and single-chain surfactants. Extending this approach by using charged lipids and biopolymers such as proteins, DNA, and polysaccharides as the polyelectrolyte offers several advantages in the areas of biotechnology, biomolecular materials, and especially gene therapy. Indeed, complexes of DNA (a negatively charged biopolymer) with cationic lipids have been proven to be an effective vehicle for the delivery of DNA into cells and are presently undergoing clinical trials. There have also been recent reports on the use of protein-cationic lipid complexes for protein delivery. Moreover, proteins are also used as target-selective agents in CL mediated delivery of DNA to cells. Since the biopolymers adopt well-defined ordered structures (a-helices, beta-sheets, double helices, etc.), the complexes in principle could form higher-ordered self-assembled structures where the biopolymers organize into liquid crystalline arrays in a self-assembled lipid matrix. Such a higher-ordered structure was recently reported by Raedler et al., who studied complexes of a linear DNA with mixtures of a cationic and a neutral lipid using high-resolution x-ray scattering. It was found that the complex adopts a lamellar liquid crystalline morphology with alternating layers of lipid bilayers and DNA. In addition, the DNA in between the bilayers was found to be ordered in a two-dimensional smectic array.

The aim of the present investigation is to systematically characterize the structure of protein-cationic lipid complexes. Only a few studies have been done on polypeptide cationic lipid complexes, and they were mostly restricted to the solid-state properties of such systems. In this study we mainly deal with the structure of these complexes in the solution state because the presence and the nature of the solvent can significantly affect the phase morphology of these systems.

Since natural proteins interact and fold specifically, depending on the exact amino acid sequence and the local environment, we chose to study a relatively well-defined model anionic polypeptide, sodium salt of PGA. Most of the experiments were carried out with a commercially available sodium salt of PGA of molecular weight 81,500. Commercially available PGA seldom has a molecular weight higher than 100,000 and is not quite monodisperse ($M_w/M_n = 1.15$). Attempts to synthesize PGA with higher molecular weights and narrower molecular weight distributions using existing synthetic methodologies have been unsuccessful. We have devised a new route to synthesize a high molecular weight PGA with M_n ~320,000 and a polydispersity of 1.06. The high-molecular-weight PGA was used to study the effect of molecular weight and the polydispersity of the PGA on the microstructure of the complexes. The cationic lipid used was a double-chained amphiphile DDAB, whose phase behavior is well known. Complexes were usually made with PGA and mixtures of the cationic lipid (DDAB) and the neutral lipid DLPC. The neutral lipid was used to systematically vary the charge density of the mixed lipid system. Both DDAB and DLPC contain 12 carbon atoms in their hydrophobic tails and are thus closely matched in their hydrophobic regions. However, the head group of DLPC is larger by 3 Å.

The structure of these complexes was characterized by small-angle x-ray scattering, zeta potential measurements, and optical microscopy.[13] X-ray scattering and small-angle x-ray scattering of these complexes revealed a multilamellar structure of the lipids with the PGA intercalated in between the layers, similar to the structure observed in CL-DNA complexes. However, there was no evidence of any in-plane ordering of the PGA molecules in contrast to the two-dimensional smectic ordering of DNA molecules found in complexes of DNA and CLs.

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Mixing Rates Radiometric Dating of Deep-Sea Corals to Determine Glacial Ocean Mixing Rates

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Abstract

Changes in oceanic mixing rates are thought to have played a key role in driving glacial-to-interglacial climate change. Deep-sea corals provide a new and unique method of documenting changes in ocean mixing rates between the last glacial cycle and the present. These corals grow on the seafloor and can be age-dated by two techniques: uranium-series disequilibrium (based on in-growth of both protactinium-231 and thorium-230) and radioactive carbon decay. Uranium-series disequilibrium dating gives the calendar or true age of the coral. Radiocarbon dating gives the age of the coral in radiocarbon years, which is offset from calendar age by changing atmospheric carbon-14 content and by the "age" of the seawater that the coral lives in. The seawater age reflects the isolation time of the water parcel from the atmosphere and is a measure of the ventilation age of abyssal waters. Using calibrations of radiocarbon-calendar age offset in the past, it is possible to convert the observed coral calendar-radiocarbon age difference into ventilation age of the water at that site.

We have determined radiocarbon and uranium disequilibrium ages on three "modern" deep-sea coral samples and three glacial-age corals. Our results for the modern corals indicate that calculated ventilation ages are in close agreement with values expected from modern hydrographic relationships. Uranium-series results for two of the glacial-age corals suggest post-depositional addition of a detrital or authigenic component which leads to discordant thorium and protactinium ages. A third samples yields concordant ages for both protactinium-231 and thorium-230 in-growth. This is the first example of a deep-sea coral age with concordant ages based on two separate uranium decay series. The ventilation age calculated from the uranium-series and radiocarbon ages is 1070 ± 130 radiocarbon years, compared with 850 ± 50 years at present. This result agrees with other research indicating reduced rates of deep-water formation in the glacial Atlantic and more sluggish abyssal circulation. If confirmed by other Antarctic corals, these results could be an important constraint on models of glacial circulation and mixing.

This project has allowed University of California researchers with expertise in paleoceanography and geochemical proxy tracers to join forces with Los Alamos National Laboratory researchers with expertise in uranium-series disequilibrium dating and high-precision thermal ionization mass spectrometry. Neither research group could have accomplished this research without the collaboration and support of the CULAR program.

Background

Changes in oceanic mixing rates are thought to have played a key role in driving glacial-to-interglacial climate change.[1] Deep-sea corals potentially provide a new and unique method of documenting changes in ocean mixing rates between the last glacial cycle and the present.[2,3] Corals contain significant concentrations of uranium, and therefore they can be dated by both radiocarbon decay and uranium/thorium and uranium/protactinium disequilibria. Radiocarbon ages of modern deep-sea corals reflect the age of the bottom water in which they grew. The age of actual coral formation (calendar age) can be precisely determined by uranium/thorium and uranium/protactinium disequilibria. In principle, the difference between these two ages reflects the age of the bottom waters the corals were living in, which can be directly related to the mixing rate of the ocean.

We have chosen to apply this approach to deep-sea corals dredged from the Southern Ocean for three reasons: the availability of well-characterized, dredged coral specimens from this region; the general importance of the Antarctic region to the modern abyssal circulation; and the current conflict between two prominent paleochemical tracers regarding the age of bottom waters in the Antarctic.[4–6] Radiocarbon dates for the Antarctic specimens that we are working on range in age from the last glacial period to the modern era; by determining uranium/thorium and uranium/protactinium disequilibria ages and radiocarbon ages on individual corals, we can determine how the age of bottom waters in the Southern Ocean has varied between climate extremes.

Progress

Our work has proceeded on two fronts: At UC Santa Barbara we are working on establishing the heterogeneity of coral chemistry, the efficacy of various cleaning methods for preparing samples for dating, and stable isotopic analyses that are required for the correction of radiocarbon dates. At Los Alamos National Laboratory, we are using the Laboratory's advanced thermal-ionization mass spectrometry facilities to perform the difficult uranium, thorium, and protactinium measurements required for disequilibrium dating.

UC Santa Barbara prepared coral specimens for the first uranium-series measurements made at Los Alamos and also made measurements of coral chemistry using a low-resolution plasma mass spectrometer at UC Santa Barbara. The work clearly demonstrated that there is small-scale heterogeneity in the distribution of uranium and other ions in the coral skeleton, that different fractions of the skeleton require different levels of purification, and that certain parts of the coral are coated with oxides of manganese that might adversely affect the uranium-series dating. Finally, a cleaning protocol was developed for the older (glacial-age) specimens so that purified fractions will yield reliable uranium-series dates.

Los Alamos has produced results for three corals that are thought to be approximately contemporary in age (i.e., living or recently alive when collected). The results are detailed in Table 1 and are extremely encouraging. To summarize, (a) deep-sea corals contain sufficient uranium (~3 ppm) for disequilibrium dating, and the isotopic ratio of that uranium indicates a seawater source with no alteration or addition; (b) both the thorium-230/uranium-234 and protactinium-231/uranium-235 ratios indicate essentially modern ages and closed system behavior; (c) thorium and protactinium ages agree within error (the larger error for the protactinium ages is due to the low activity of uranium-235); and, (d) ventilation ages, calculated as the difference between the thorium age and the carbon-14 age, increase with water depth exactly as expected, because deep waters have been isolated from the

Location	Depth (m)	U (ppm)	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{231}Pa/^{235}U$	Th Age	Pa Age	^{14}C Age	Vent Age
53°S, 75°W	97	3.27	1.1497	0.000637	0.0022	70 ±10	100 ± 50	520	520
51°S, 162°E	352	3.43	1.1469	0.000623	0.0042	70 ± 5	200 ± 50	670	670
42°S, 176°E	949	2.92	1.1447	−0.00038 [a]	−0.0017 [a]	−40 ±190	−80 ± 50	810	810

[a] The negative ratios for the third sample occur because the measured Th and Pa levels were below the bank level. This sample has no measureable Th or Pa in-growth and therefore is of zero age.

Table 1. Measurements and ages of three corals.

atmosphere for a longer period and therefore show increasingly older carbon-14 ages.

These first results are extremely encouraging because they confirm three key tenants of our initial hypothesis. First, deep-sea corals can be dated by both radiocarbon and uranium-series disequilibrium. Corals behave as a closed system chemically and do not appear to incorporate extraneous thorium or protactinium, which would confound uranium-series dating. Finally, modern corals yield ventilation ages that are consistent with their depth distribution.

Subsequent to our successful dating of contemporary corals, we turned our attention to relict specimens of deep-sea coral that have been dated by radiocarbon to the last glacial period.[7] We have made substantial progress toward this goal. Three glacial-age coral specimens were identified by radiocarbon dating at Lawrence Livermore National Laboratory and selected for uranium-series disequilibrium dating. Two sets of samples were prepared at UC Santa Barbara from each specimen: raw untreated coral material and coral material that was taken through a rigorous set of physical and chemical purification steps to remove contaminating phases. These fractions were then analyzed for uranium, protactinium, and thorium at Los Alamos by thermal ionization mass spectrometry.

Results from the analyses revealed that two of the three selected coral specimens had experienced alteration or open-system behavior. (Other laboratories have reported similar results.) Alteration was indicated by slightly elevated uranium-234/uranium-238 ratios and high (detrital?) thorium contents (~2 ppb). One of these samples (No. 47406) yields discordant thorium and protactinium ages even when the "clean" fraction ratios are corrected by using the "dirty" (untreated) fractions. The other sample (No. 47395) yields concordant thorium and protactinium ages, but the age of the sample is greater than the radiocarbon age, which is physically implausible. However, the detrital correction applied to this sample is based on another sample, so obtaining a uranium-series date on an uncleaned fraction will allow us to correct this date.

Three fractions analyzed from a third sample (No. 47396) yielded far more promising results: uranium-234/uranium-238 ratios consistent with unaltered seawater, low thorium contents, and ages that required only small corrections. The corrected ages, based on comparison of clean and dirty coral fractions, are 16,600 ± 210 years BP for uranium-protactinium and 16,520 ± 210 years BP for uranium-thorium. This is the first time that radioactive dating of a glacial age deep-sea coral has yielded reliable (concordant) results based on two independent uranium-series decay chains. The radiocarbon age of this sample is 15,280 years BP.

We apply the following method to convert the age determinations into ventilation ages: The uranium-thorium-protactinium age of the coral is taken as the calendar (i.e., true) age of the sample. Using a marine surface coral carbon-14–calendar age calibration, we calculate the expected surface water radiocarbon age of the sample, which is 14,210 years BP. The offset between the calculated age and the observed radiocarbon age of the coral is equal to the warm surface water to deep water radiocarbon offset during the glacial. This value is approximately equal to the ventilation age (an exact treatment requires taking into account changing atmospheric radiocarbon during the time the water mass is isolated). For sample 47396 (Drake Passage: 59°44′S, 68°51′W, 1042–1207 m) we calculate a ventilation age of 1070 ± 130 radiocarbon years. The modern radiocarbon ventilation age at this site is 850 ± 50 radiocarbon years. Our data indicate a significant increase in mixing time, consistent with a variety of evidence suggesting diminished rates of deepwater formation in the glacial North Atlantic.[8] Our calculated radiocarbon age is approximately equal to a calendar-year ventilation age of 1240 years. The calendar age ventilation age is considerably larger because of the increasing difference between radiocarbon age and calendar age over this time interval.[9]

Implications of Our Research

Integrating our work into a broader context, we compare our calculated ventilation age with two previously reported values for the North and tropical Atlantic (Fig. 1). This comparison demonstrates that all three sites record increased ventilation ages for glacial age corals.[2,3] In fact, the upper limit for the ventilation ages at all three sites is about 1200 years, suggesting that for at least some part of the last glacial maximum, the Atlantic and Antarctic basins were dominated by bottom waters of the same age. This conclusion agrees with previous studies based on isotopic and trace metals preserved in foraminifer shells.[4,10-12] The present-day Atlantic is filled by relatively "young" waters with typical ages of about 400 years.[13] The young age of Atlantic bottom waters relative to the Pacific and Indian Oceans reflects the rapid ventilation of the Atlantic via the Nordic Seas.

Our results agree with previous inferences which suggest that convection in the Nordic Seas was much weaker during the last glacial maximum, leading to a rise in the nutrient content and age of glacial bottom waters.[8,14,15] Our results are the only determination of mixing age for glacial Antarctic water. If they are confirmed by other Antarctic corals, they will be an important constraint on models of glacial circulation and mixing.[2]

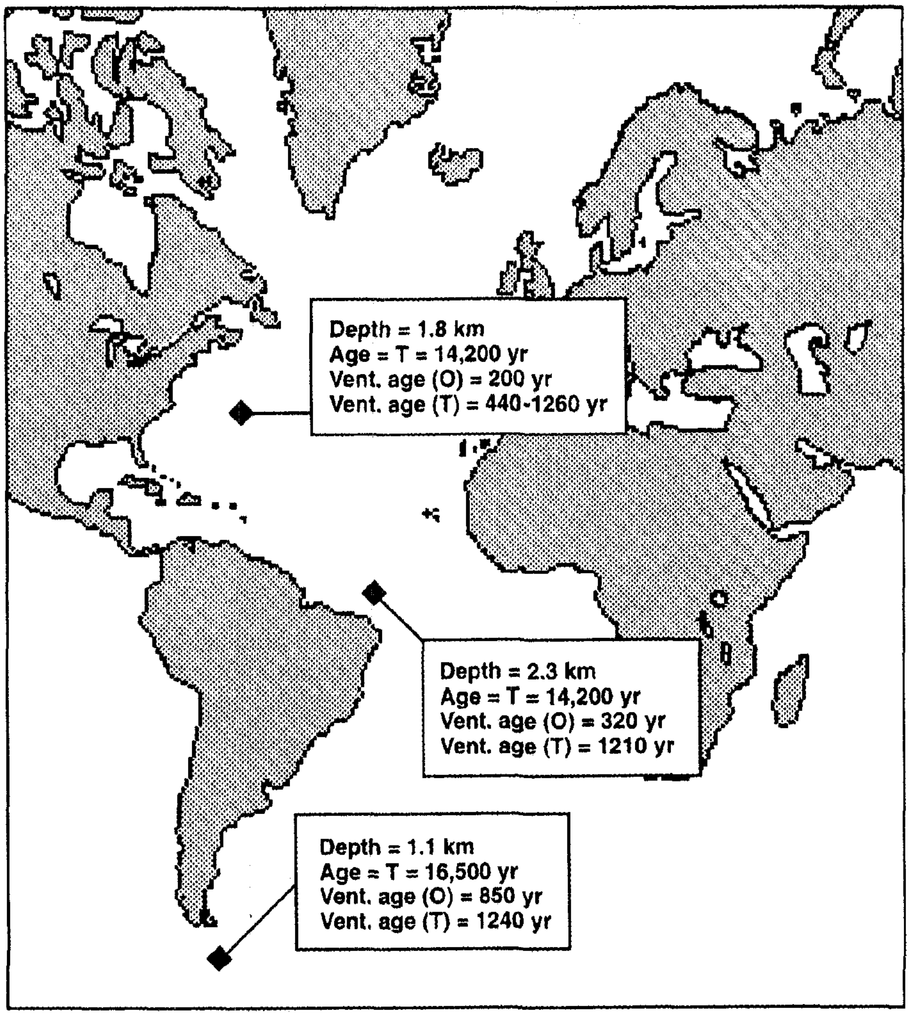

Fig. 1. Our calculated ventilation age is compared with two previously reported values for the Atlantic Ocean.

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Goldstein, S.J., D.W. Lea, M. Kashgarian, M.T. Murrell, A.J. Nunn, and S. Chakraborty "^{231}Pa and ^{230}Th Dating of Deep Sea Corals from the Last Glacial Period," Los Alamos National Laboratory document LALP 97-99 (1997) p. 40.

Tudhope, A.W., M.T. McCulloch, C.P. Chilcott, G.B. Shimmield, D.W. Lea, and J. Chappell, "ENSO-Style Climatic Variability during Interglacial and

Glacial Regimes: Evidence from Living and Late Quaternary Annually-Banded Massive Corals in Papua, New Guinea," in *Global Changes and Their Significance for the Future* (University of London, UK, 1998).

Tudhope, A.W., C.P. Chilcott, M.T. McCulloch, J. Chappell, G.B. Shimmield, R. Ellam, and D.W. Lea, "ENSO-Style Climate Variability during Glacial and Inter-Glacial Climate Regimes: Evidence from Massive Corals in Papua, New Guinea," *EOS, Transactions of the American Geophysical Union* 79 (45), F493 (1998).

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Goldstein, S., M. Murrell, D. Lea, S. Chakraborty, and M. Kashgarian, "^{231}Pa and ^{230}Th Dating of Deep Sea Corals," Meeting of the American Geophysical Union, San Francisco, CA, December 15–19, 1996 (contributed).

Goldstein, S.J., D.W. Lea, M. Kashgarian, M.T. Murrell, A.J. Nunn, and S. Chakraborty, "^{231}Pa and ^{230}Th Dating of Deep Sea Corals from the Last Glacial Period," Third Alfred O. Nier Symposium on Inorganic Mass Spectrometry, Durango, CO, May 1997 (contributed).

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Charge Transfer at Conjugated Polymer/Metal Interfaces

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Abstract

The primary technical focus of this program is to measure the transport of charged carriers through tailored conjugated polymer/metal interfaces. Conjugated polymers have attracted considerable recent attention because of their technological promise for electroluminescent display and other large-area electronics applications. We are exploiting the recently developed Ballistic Electron Emission Microscopy (BEEM) technique to perform the first studies on the transport of charged carriers across buried polymer/metal interfaces as a function of electron injection energy. Over the last few years, BEEM has been shown to be a powerful probe of transport at the interface between inorganic semiconductors and metals.

This will be the first BEEM investigation of the interfaces between organic materials and metals. In this program we have established the sample preparation techniques necessary for BEEM studies of Au/MEH-PPV/Al and Au/PPV/Al devices with gold as the top electrode and aluminum as the bottom electrode. We have modified our BEEM electronics to apply external electric fields, which reduces the effects of charge trapping, and we have seen the effects of external bias on the BEEM current in GaAs Schottky diodes. We have designed an ultrahigh-vacuum BEEM system which will prevent diode degradation and allow the use of reactive metals such as aluminum and calcium with widely different work functions. We have performed the first BEEM measurements on GaN, which is a member of an exciting new group of electronic materials, the group III nitrides.

A working BEEM apparatus that can study modulated BEEM has been set up at Los Alamos and used both to measure derivative BEEM spectroscopy and to measure BEEM spectra under external voltage bias. We have developed a new theory of BEEM based in electron scattering at the metal/semiconductor interface, which accurately describes measurements of a nonepitaxial systems. We have completed a systematic BEEM study of AlGaAs/GaAs heterostructures buried below a Au/GaAs interface and used theory that we developed to successfully describe these measurements.

Background

The formation of semiconductor interfaces

and a description of their characteristics is a problem of long standing in condensed matter physics. Understanding of the mechanism of interface formation, the Schottky barrier at metal/semiconductor (MS) interfaces and semiconductor heterostructure band alignments, is fundamental in determining carrier transport through such structures. The electrical properties of such structures are clearly of importance in the operation of most electronic and optical devices.

The characterization of such interfaces has traditionally been done through electrical probes such as current-voltage and capacitance-voltage techniques. These are gross techniques that measure an ensemble average in space over an ill-defined range of carrier energy. Scanning tunneling microscopy (STM) enables the investigation of the surface electrical properties of conducting materials with high spatial and energy resolution. BEEM, a closely related technique has recently been used to investigate subsurface electronic properties, primarily at MS interfaces.[1]

In BEEM, an STM tip is used to inject hot carriers into a thin metal layer deposited on a semiconductor. The metal layer (base) is used as a contact for STM feedback to keep a constant tunneling current. A fraction of the injected carriers travel ballistically through the metal layer to the MS interface. Carriers with sufficient energy and the appropriate momenta can overcome the Schottky barrier and enter the semiconductor where they are collected and measured as a BEEM current. A schematic energy level diagram for BEEM is shown in Fig. 1.

Since the observation that conjugated polymers can serve as the active medium for light-emitting diodes (LEDs),[2,3] the electronic and optical properties of these materials have become of great interest. Conjugated polymers possess significant advantages over conventional inorganic semiconductors for LED applications. The emission spectra of conjugated polymers can be tuned throughout the entire visible region of the spectrum by modifying the molecular structure of the polymer.
High-quality thin polymer films can be fabricated by spin casting, and devices can be easily delineated using optical lithography. These fabrication advantages will be of great importance for display manufacturing.

In recent work at Los Alamos, the relative energy levels at the interface between the polymer poly[2-methoxy,5-(2'/-ethyl-hexyloxy)-1,4-phenylene vinylene], or MEH-PPV, and various metals have been studied by using internal photoemission and electroabsorption.[4] The energy barrier to charged carrier injection was found to vary directly with the work function of the metal. Thus, electrons are easily injected into the polymer from small work function metals, and holes are easily injected from large work function metals. We are using the information obtained by Los Alamos on the energy positions at metal/MEH-PPV interfaces to design our initial BEEM experiments.

Because of its inertness and because an extensive amount of BEEM work has been done using gold films on inorganic semiconductors, we choose gold to be the top contact. The lower work function metal, aluminum, is chosen as the bottom contact to minimize leakage currents. MEH-PPV and PPV will be the polymers used in the first experiments. The thickness of the polymer film will be between 10 and 50 nm. This thickness is chosen to maximize the transport of charge across the polymer for collection and at the same time to minimize leakage due to pin holes in the polymer film. Recent internal photoemission experiments at Los Alamos have shown that a photon flux which would correspond to an effective tunneling current of about 40 nA in a BEEM experiment gave a detected photocurrent, which would correspond to the BEEM current, of about 10 pA. These currents are adequate for a successful BEEM experiment.

Unlike inorganic semiconductors, the mobility of carriers in polymers is quite low so that the transit through the polymer must occur by drift rather than diffusion. The use of asymmetrical metal contacts leads to a built-in electric field. The energy level diagram for a MEH-PPV structure with gold and aluminum contacts is shown in Fig. 2.

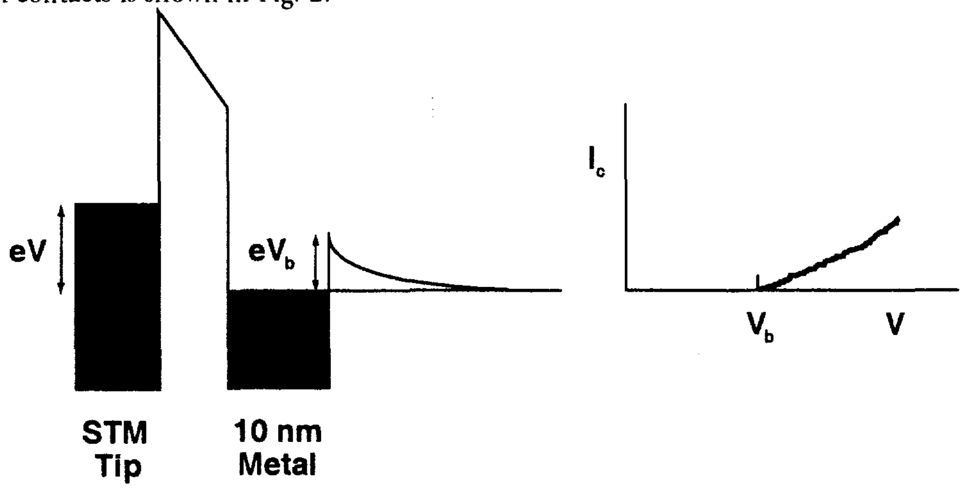

Fig. 1. Schematic energy-level diagram of a BEEM experiment for a tip bias (V) greater than the Schottky barrier height (eB_v) *(left) and a schematic of BEEM collector current* (I_c) *as a function of tip bias (right).*

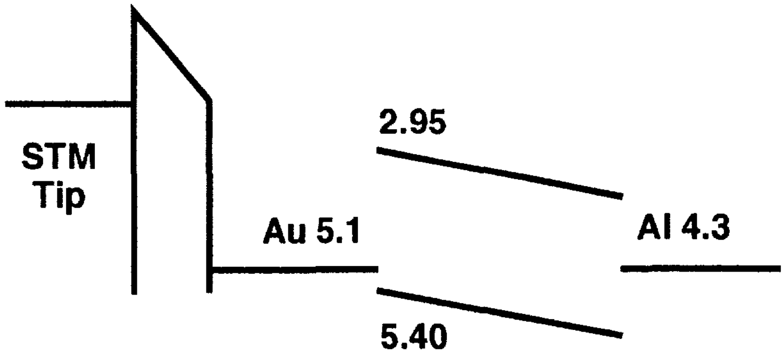

Fig. 2. Energy-level diagram for a BEEM experiment on a MEH-PPV structure with gold and aluminum contacts. The built-in field that is due to the work function difference between gold and aluminum is used to collect the electrons injected in to the MEH-PPV by the STM tip. Energies are in electron volts.

The group III nitrides have recently been shown to be highly efficient light emitters in both the green and blue spectral regions. Efficient LEDs and, very recently, injection lasers have been fabricated from these materials. The electrical and optical properties of these materials are still poorly understood. The application of BEEM techniques to understand these materials is an extremely timely topic.

Benefits to Los Alamos and UC Santa Barbara

We expect that the work undertaken in this program will provide the basic scientific understanding of interfaces which contain an organic electronic material as a constituent. Such interfaces are the essential element of organic electronic and electrooptic devices. We will establish the basic principles governing the electronic properties of these interfaces. These principles will form the scientific basis for organic electronic material and device design. They will provide the fundamental understanding needed to intelligently design organic materials at the molecular level and devices at the mesoscopic level for electronic applications. Organic electronic materials and devices are going to start a revolutionary new electronics technology. The work undertaken here will provide the scientific basis for this technological revolution. The electronic materials research groups at Los Alamos and UC Santa Barbara will be at the forefront of this rapidly expanding new field.

Progress

The mobility of carriers in polymers is quite low and the injected electrons must transit through the polymer by drift rather than diffusion. Our initial experiments, done under ambient conditions, have been limited to the use of gold as the top electrode and aluminum as the base and have necessarily involved electron injection. These have yielded inconclusive results that are due to the trapping of the electrons and the small built-in electric fields that are a consequence of the limitations of metal electrodes possible in non-ultrahigh-vacuum (non-UHV) BEEM. The following three steps are necessary to successfully apply the BEEM technique to polymer devices:

1. An externally applied bias like that in the internal photoemission experiment will force a current through the polymer and neutralize the charge traps. It will then be possible to detect a small collector current caused by injected charge carriers that made it over the Schottky barrier and through the polymer. Applying an external bias would also make it possible to measure the electronic behavior of the same sample for electrons and holes.

2. The polymer LEDs are very leaky diodes. At externally applied electric fields of the order of 10^5 V/cm, leakage currents are much higher (μA) than the expected collector current (pA). Therefore, it will be necessary to use lock-in techniques to detect the signal. We are planning to modulate the tunneling current of our BEEM system by modulating the tunneling voltage.

3. We intend to do the measurements in a UHV environment. This will allow us to use different metal combinations in the metal/polymer/metal structure (e.g., aluminum or gold as base electrode on top of the structure) with the possibility to investigate hole injection in addition to electron injection. In addition and very important, the polymer material does not deteriorate so fast when it is not exposed to air during the measurement.

UC Santa Barbara researchers have worked closely with Los Alamos to develop the sample preparation techniques and to do initial BEEM measurements on Au/MEH-PPV/Al and Au/PPV/Al diodes. We have completed the following activities.

1. We have modified the BEEM electronics so that an external bias can be applied to the sample. The external bias circuit on a $Al_{0.3}Ga_{0.7}As$ single-barrier structure has been successfully tested. These are the first measurements of BEEM in this system with an external applied field. This measurement gives us confidence that we can now proceed to apply modulating signals to the tunneling current to further enhance BEEM capability for the study of polymer diodes.

2. Researchers at UC Santa Barbara have designed a UHV low-temperature BEEM system. This system is currently being built by Surface/Interface Inc. and is expected to be delivered this fall. The UHV capability should aid greatly in exploring other metal combinations such as aluminum on top and also allow the study of hole injection in complete analogy to the internal photoemission

measurements performed at Los Alamos.[4]

3. BEEM has been applied to study GaN for the first time; GaN is a member of the group III nitrides, an exciting new class of electrooptic materials.

4. A working BEEM apparatus which can study modulated BEEM has been set up at LANL and been used to measure both derivative BEEM spectroscopy and to measure BEEM spectra under external voltage bias.

5. We have developed a new theory of BEEM based in electron scattering at the MS interface that accurately describes measurements of nonepitaxial systems.

6. We have completed a systematic BEEM study of AlGaAs/GaAs heterostructures buried below a Au/GaAs interface and used theory that we developed to successfully describe these measurements.

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Photolithographic Immobilization of Biopolymers: Breaking the Diffraction Limit

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Abstract

There are many areas of biochemistry and biomedical research that would benefit from ultratrace analyses (a few thousand molecules) of very small volumes (less than a microliter). The analysis of single mammalian cells and clinical bioassays are just two examples. The intent of this application is to demonstrate the feasibility of preparing arrays of sensors, each component of which has submicron dimensions. This will allow the measurement of a wide variety of biological analytes with only picoliter quantities of sample. The best way to generate these sensors involves the use of photolabile protecting groups, good chromophores that are very light sensitive, that can be incorporated into the surface derivatization chemistry. These groups can be photolytically cleaved from specific regions of the substrate surface by applying appropriate wavelengths of light. This chemistry has been exploited commercially with conventional masking technology to obtain biopolymer structures with dimensions of 100 μm on a side. In the work proposed here, near-field scanning optical microscopy (NSOM) will be used to fabricate biopolymer arrays with dimensions on a submicron scale using biotin/avidin technology. This will allow the production of enzyme-based sensors so that products can be monitored with fluorescence microscopy and/or affinity-based sensors so that binding reactions are monitored by fluorescence with NSOM with 0.1-μm resolution.

Background

This work describes the development of a protocol for the submicron spatial segregation of multiple biosensor sites onto a single substrate. This would improve the spatial resolution of array-based sensors by well over two orders of magnitude in each dimension and would allow the analysis of samples that could not be analyzed with conventional methods. The preparation of an array of submicron sensor elements, each component of which has different selectivity and submicron dimensions, will allow the measurement of a wide variety of biological analytes with only picoliter quantities of sample. This would be extremely useful for the analysis of complex and very small biological samples such as a pediatric blood sample. Here, an array of antibodies with different affinities would allow a complete blood analysis (involving 256 analytes) to be run on a sensor surface less than 10 μm^2 with a total sampling volume of about 1 picoliter (10^{-15} L). Alternatively, one could read an array of submicron sensor elements with the same selectivity to gain extremely high spatial resolution of the distribution of a single component. An example of this would be the secretion of a neurotransmitter from a single nerve cell. A cultured neuron could be placed onto the sensor array and stimulated, and the pattern of secretion could be established by monitoring the discrete sensor elements within the array.

Thus, it seems clear that this technology will have a significant impact in many modern areas of biology and medical science.

Nanopatterning for biosensors. Ultrahigh-resolution photolithography will be used for biosensor development on the submicron scale. Experiments are aimed toward generating microscopic regions with a specific type and density of surface functionality to provide a surface that is optimized for detection of extremely small quantities of analytes (attomole to zeptomole) in very small volumes of sample (picoliter to femtoliter). The spatially localized modification of a sensor surface (e.g., an optical fiber) is proposed with subdiffraction limited optics to allow spatial segregation of biopolymer-binding sites. Similarly, bioassay chips will be developed to screen peptides for drug development and for analyzing oligonucleotides for DNA sequencing. These chips will be photolithographically formed by additively synthesizing complementary peptides or oligonucleotides in an array of small areas (approximately 1 μm^2) on a chip.

Nanopatterning of biopolymers will be accomplished by means of two technologies:

(1) Spatial segregation will be accomplished using nanophotolithographic removal of protecting groups inserted at specific steps in the chemical derivatization procedure.

(2) Biotin/avidin technology will be combined with latex nanostructures (20 to 200 nm in diameter) to increase the effective surface area for biopolymer loading on the sensor. The specific modifications of submicron regions of the sensor surface will be characterized routinely with fluorescence microscopy using a cooled charge-coupled device (CCD) imaging system to visualize the spatial distribution of biopolymer immobilization sites (as indicated by emission from fluorescently tagged substrates). Even greater spatial resolution will be obtained through the use of near-field scanning optical microscopy (NSOM), when subdiffraction limited optics will provide images with 100-nm resolution and single-molecule sensitivity.

Nanophotolithographic immobilization of biopolymers on glass surfaces. Photolithography has been used extensively in the formation of electronic circuits and optical gratings, and more recently, it has been used in the construction and design of templates for the parallel synthesis of peptides and oligonucleotides.[1] Spatial control of the derivatization of solid substrates has been achieved through the use of photolabile protecting groups, where such groups are removed after application of an appropriate wavelength of light to allow activation of a specific chemical synthetic step.[2] Photolabile protecting groups, which are good chromophores that are very sensitive to light, must be relatively stable to the other chemical reagents so that they will be exposed to in the ground state as part of the synthetic procedure.[3] The selective removal of these photolabile groups has been directed through conventional masking technology to obtain structures with dimensions of 100 μm on a side.[2]

We intend to use similar chemistry to fabricate arrays with dimensions on a submicron scale. Reactive groups at any stage in the derivatization procedure (e.g., silanols, amines, etc.) on the glass surface can be labeled with a protecting group that will prevent further derivatization. A typical protocol that involves protection/deprotection of the amine tether involves the formation of a 1-(2-nitro-4,5-methylenedioxylphenyl)ethyl-1-chloroformate (MeNPOC) derivative of the amine, prepared by reaction of free amino terminals of all surface-attached amines with MeNPOC.[4] Spatially regionalized illumination of the MeNPOC-derivatized amine with ultraviolet (UV) light results in photolytic cleavage of this group only in those sites exposed to light, forming the primary amine and allowing the reaction sequence to continue only in those "deprotected" regions.[5] The deprotected amines can then undergo the conventional reactions with NHS-biotin, avidin, and the biotinylated enzyme. This attaches the enzyme to the surface only in those regions that have been illuminated with UV light. Since there is a wide variety of photolabile protecting groups available for the modification of amines,[3] the choice of the protecting group will depend on the nature of the protected group and the wavelength of light to be used. We will investigate the use of these protecting groups, as well as many others, at various stages in the derivatization procedure.

Characterization and readout of derivatized surfaces. We have demonstrated that fluorescence microscopy can be used to provide a two-dimensional image of the distribution of various chemical functional groups across modified carbon electrode surfaces.[6–8] CCD cameras are very sensitive light-gathering devices, and the small pixel size of the CCD can be used to great advantage when combined with fluorescence microscopy, such that spatial resolution near the diffraction limit of the light used (0.5 μm) can be obtained. At Los Alamos, we have the capability to obtain subdiffraction-limited resolution (0.1 μm) and single-molecule sensitivity with NSOM.[9–11] This will allow the quantitative characterization of submicron structures created at every step in the derivatization process and will allow complete optimization of the immobilization procedure. Ultimately, NSOM will be used as the readout device to measure the quantity of fluorescently tagged substrate bound to a surface-attached probe in affinity-based sensors. Thus, we are uniquely capable of characterizing these minute structures both qualitatively and quantitatively.

Progress

The analysis of very small and complex biological samples with biosensors has been the focus of much analytical research in recent years.[12–14] The construction of arrays of micron dimension sensor elements, each with different selectivity, would allow the measurement of many different biological analytes, such as those contained in a pediatric blood sample with only picoliter quantities of sample. Spatial segregation of biosensor elements can be achieved with photocleavable reagents that are used to protect or deprotect derivatization sites on carbon or other substrate surfaces. Photodeprotection has been widely used to control spatial segregation of biomolecules, chiefly by activation of photosensitive reagents to immobilize proteins.[15]

Subsequent attachment of proteins has been performed with well-characterized biotin/avidin chemistry.[15] The binding of streptavidin, a tetramer protein that binds four biotin molecules, is comparable in strength to a covalent bond ($K_a = 1 \times 10^{15}\ M^{-1}$).[15,16] Once formed, the complex is stable under conditions of extreme pH, temperature, and organic solvents or denaturing reagents. The multiple binding sites of avidin for biotin allows for construction of biotin-avidin-biotin "sandwiches" that can be derivatized with biotinylated enzymes or other biosensor elements.

To combine photolithography and biotin/avidin technology, we have used a photoactive form of biotin. Photobiotin, a nitro(aryl) azide derivative of biotin, has been used for protein and nucleic acid labeling.[17,18] Upon exposure to UV light, a photochemical reaction occurs that generates a nitrene, which inserts into C–H and other chemical bonds. Photolithographic masks have been used to create surface-bound antibody sites with spacing of 1.5 μm (Ref. 19). It has also been demonstrated that photobiotin will bind covalently to an organic surface when exposed to UV light.[20] Polystyrene or nitrocellulose substrates were exposed through a mask to create patterns that were 600 μm on a side. Previously in this laboratory, a laser interference pattern was used to immobilize 5-μm-wide lines of photobiotin on glassy carbon surfaces.[21] Biotinylated alkaline phosphatase

(ALP) was bound to the exposed lines by means of a biotin-avidin-biotin linkage. The lines were imaged by adding a substrate that was converted to a fluorescent product by the ALP.

Confocal microscopy has become widely used in three-dimensional imaging in recent years because of its excellent lateral resolution and sectioning capabilities.[22] In contrast to conventional wide-field microscopy, the field of illumination in confocal microscopy is confined to a diffraction-limited spot with a diameter as small as approximately half the wavelength. The objective projects an image of the illuminating spot into the sample, thus illuminating only a small region. By moving the light source or the sample, specific regions of the sample can be illuminated and sampled. Typically, a pinhole is placed in front of a photodetector to detect only the reflected light or fluorescence that is in the focal plane of the objective, thus eliminating out-of-focus light. Confocal imaging has been used in the medical field to image a wide variety of samples such as kidney sections.[23] Confocal microscopy has also been used for its spatial and depth resolution to image surfaces and surface phenomena. For example, localized corrosion, copper electrodeposition, adsorption of organics,[24] and electroetching[25] have been investigated using confocal laser scanning microscopy. In addition, the small probe volume produced by spatial filtering can be used to lower background scatter enough to detect single fluorescent molecules.[26]

In this work, a laser source focused through a quartz microscope objective was used to initiate the reaction and immobilization of photobiotin to glassy carbon and fused silica surfaces. The small area of illumination from the objective lens at the focal point allows spatial control of derivatization when sample movement is controlled in three directions by a piezoelectric positioner. Line patterns of immobilized photobiotin with widths of 5 to 20 µm were produced by positioning the sample surface in the focal plane of the microscope objective and subsequent exposure of the surface at varying scan speeds (Fig. 1). Fluorescently tagged avidin was then attached to the patterned biotin surface and visualized using fluorescence microscopy and a cooled CCD system (Fig. 2). The variability of biotin deposition and the subsequent binding of fluorescently labeled avidin were characterized.

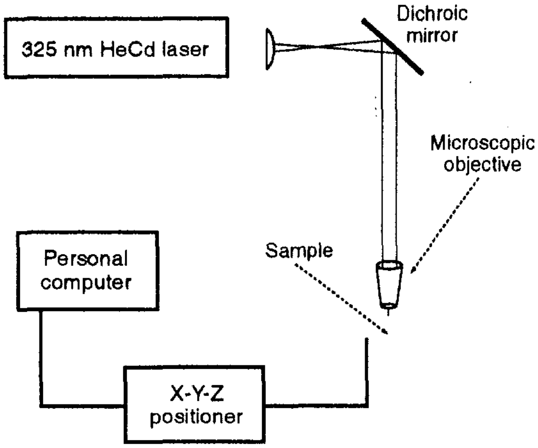

Fig. 1. Simplified diagram of a laser scanning confocal microscope.

UV immobilization of photobiotin on fused silica surfaces was investigated at Los Alamos. Several letters were UV-written into the interface between the photobiotin and the APTES/fused silica layers and subsequently derivatized with TX-Red avidin. Letters were selected to spell out our institutional acronyms—LANL and UCR. The letters were 25 µm high, with line widths of 5 to 10 µm. As can be seen in Fig. 2, other spots of fluorescence were present in addition to the patterned letters. The spots result from nonspecific binding of TX-Red avidin to the fused silica surface, which was more prevalent on the APTES/fused silica compared with glassy carbon. This figure does, however, serve to illustrate that this form of photolithography can be used to write structures on a glass surface as well as on carbon.

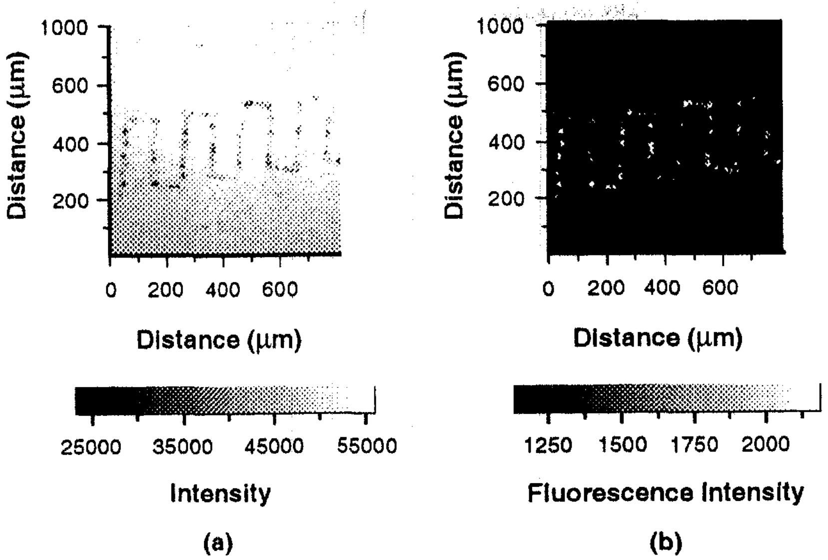

Fig. 2. White light reflectance (a) and TX-Red avidin fluorescence (b) images of photobiotin immobilized on glassy carbon with the laser focused through a 25 × 0.5 N.A. microscope objective. Magnification for these images was 5×. The sample was moved in a raster pattern at a scan rate of 75 µm/s.

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Investigation of Trans-Ionospheric Pulse Pairs (TIPPs)

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Abstract

The small "micro" spacecraft ALEXIS carried a broadband radio detector nicknamed Blackbeard, which discovered extremely intense pairs of radio signals in the 10s to 100s MHz band. The only natural process that could cause such a signal was electrical discharge from storm clouds. However, a variety of discharge phenomena are present in clouds. There are discharges to the ground, discharges that remain within the cloud, and discharges to the ionosphere. This study focused on determining whether the signals were natural in origin and, if so, which cloud-discharge process was responsible. The geographic distribution of the signals showed that they were produced over continents in the lightning-producing belts. These regions moved with the season just as lightning activity is known to do. The diurnal variation was similar to that of cloud-to-ground lightning but not identical. Comparisons of the time and place of occurrence with those of various forms of lightning detected by the ground-based stations of the National Lightning Detection Network (NLDN) showed that the signals were coincident with internal discharges in clouds. One event from an ordinary-size storm was located with the NLDN data at the time of the detection by Blackbeard, and these data were used to show that the two pulses in a trans-ionospheric pulse pair were separated by the time required for the second signal to bounce off the surface of the earth. Later, in a study of a powerful hurricane, Fausto, more signals were geolocated in the storm's central region at rather high altitudes, 12 to 17 km.

This study is important to the Laboratory because this frequency band is used for communication, and we need to know the intensity and occurrence of signals in this band that might interfere with or be mistaken for man-made signals. Furthermore, it provides more understanding of a most powerful process occurring near the very tops of clouds.

Background

Recently, there has been an explosion in research related to the topic of "upward lightning." Observations of Red Sprites, Blue Jets, and gamma-ray bursts all indicate that at times strong coupling occurs between thunderheads and the ionosphere, resulting in these various phenomena. Very high frequency (VHF) radio bursts, known as trans-ionopheric pulse pairs (TIPPs), have been observed with the Blackbeard receiver on board the ALEXIS (array of low-energy x-ray imaging sensors) spacecraft. It was thought to be possible that these signals were radiation-generated by the accelerated electrons or that they could be electromagnetic radiation from lightning itself. It was also important to be able to distinguish between natural and man-made emissions as the source of TIPPs for nuclear test ban treaty purposes. We made this determination using data from the ALEXIS spacecraft, together with ground-based lightning data. TIPP characteristics provided important clues about the processes responsible for their generation, and showed that these signals arose high in the clouds in very powerful storms. This was an important collaboration for both Los Alamos National Laboratory and UC Los Angeles because it enabled the scientific fruits of the earlier mission, ALEXIS, to be harvested while Laboratory personnel were engaged almost fully with preparation of the follow-on mission FORTÉ (fast on-orbit recording of transient events). This study provided a good solid floor for the advances that are now being made with the FORTÉ mission. It also provided a University student with excellent material for a Ph.D thesis and provided a good intellectual exchange between the scientific personnel of the Laboratory and the University.

Progress

Our investigation of the geographic and seasonal variation of TIPPs included a comparison between the TIPPs as observed with the Blackbeard instrument on ALEXIS and the lightning as observed by the optical transient detector (OTD) on a separate low-altitude spacecraft. TIPPs are observed as pairs of pulses in the VHF radio band, whereas the OTD observes the optical signature of lightning. Both TIPPs and lightning show the same general geographic distribution. There is an apparent gap in TIPP occurrence over South America, but this is due to sampling bias.

We have also performed a comparison between TIPPs and lightning on a seasonal basis, from data acquired over the continental United States. We found that both lightning and TIPPs show the same general seasonal variation, with their occurrence being largest in the summer months, and decreasing in the fall. Thus, in terms of geographic and seasonal dependence, both TIPPs and lightning have the same variations, and TIPPs are a lightning-related phenomenon, in that both are generated as a result of electrodynamical processes within the atmosphere.

To determine more completely the relationship between TIPPs and lightning, we compared TIPP occurrence with lightning as detected by the National Lightning Detection Network (NLDN). The NLDN data consisted of both raw and triangulated data acquired from a large array of electromagnetic-wave field detectors. The raw data include all lightning strokes as detected by the NLDN stations, both intracloud and cloud to ground, whereas the triangulated data were reduced to the individual cloud-to-ground strokes. In the raw data, any one cloud-to-ground stroke was detected at many NLDN stations. On the other hand, intracloud lightning is usually detected at only one station. In our investigation of the diurnal variation of TIPPs, we used the triangulated data, as these are more extensive, whereas the raw data were used in case studies.

We found that while TIPPs and lightning both exhibit diurnal variation, TIPPs generally lag lightning by a few hours. Lightning tends to peak in occurrence in the late afternoon and early evening. TIPPs, on the other hand, peak near midnight. Thus, whereas the geographic analysis shows that TIPPs and lightning are related, the diurnal analysis suggests that TIPPs are not the VHF signature of a cloud-to-ground stroke. Rather, TIPPs appear to be caused by a separate electrification process. One aspect we could not examine with the Blackbeard data from ALEXIS was the effect of the background noise that was due to anthropogenic sources that too have diurnal variations. The differences in diurnal variation over North America and Africa suggest this is a possible concern. This possibility can be checked on the FORTÉ mission. To further our efforts in determining the TIPP generation process, we compared TIPPs with the raw

NLDN data. We found that for a superposed epoch analysis based on 18 TIPP events, a positive intracloud (+IC) lightning stroke is detected by the NLDN within 10 ms of 7 of the TIPPs. Moreover, of these 7 TIPPs only one event is detected at more than one NLDN station. Through analysis of the likelihood of coincidence, we have a greater than 99.99% confidence that the correlation is not random. Furthermore, the occurrence rate of +IC strokes is essentially constant, except for the single isolated peak just before the TIPP. This suggests that the signal identified as a +IC stroke is actually the ground detection of a TIPP. What distinguishing characteristics, if any, separate this type of +IC stroke from any other has not been determined. Further study of this correlation is clearly warranted, as this may provide an important clue to the TIPP generation mechanism.

One other aspect of the comparison with the raw NLDN data is that the +IC stroke coincident with a TIPP is generally detected at only one ground station. Thus, we can localize the TIPP source. The separation time between pulses could be a characteristic of an intrinsically double-pulsed signal, or it could be due to the reflection of a single pulse off the ground. Having determined a location for the source of a TIPP, we can use the pulse separation time to infer a height for the source, assuming that the second pulse has reflected off the ground. We find that the height of the source is around 10 km, consistent with a source in the cloud top. Because it is unlikely that the double-pulse mechanism would result in an apparent height equal to the cloud height, this observation provides a consistency argument in support of the ground-plane reflection model.

In two studies we were able to find ground records from the NLDN that had time of arrivals of the same intracloud pulse at two or more stations. The first of this was from a normal storm over the central United States. The observation at the two stations allowed a location of the source to be determined, and the TIPP separation provided the altitude of close to 8 km, very high in the cloud. In the second case study, multiple detections of pulses from hurricane Fausto enabled the source for the TIPPs to be determined high in the clouds, 12 to 17 km above the surface of the earth.

Clearly, we achieved the goal of the study to determine what phenomenon in clouds was associated with TIPPs. In fact, we went beyond this goal, finding both the specific pulse responsible for a particular TIPP and determining its latitude, longitude, and altitude in the cloud. Unexpectedly, these pulses occur at the highest altitude in the clouds. Since these pulses are the strongest emitters of VHF radio frequencies, our study has shown that the tops of clouds are home to previously unsuspected, powerful electric discharges.

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Modeling of Deformation, Stress, and Temperature in Subducting Slabs: Deciphering the Mechanism of Deep Earthquakes

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Abstract

The cause of deep-focus earthquakes is a major puzzle in geodynamics because at great depth rocks should flow rather than break to relieve stress. In general, failure can occur by either brittle fracture or ductile flow. Fracture and frictional sliding are strongly inhibited by pressure, but not by temperature, because they involve the opening of tensile microcracks. The stress at which rocks flow, on the other hand, is strongly reduced by increasing temperature but is essentially unaffected by pressure, because motion of crystal dislocations is thermally activated. Thus, because temperature and pressure increase with depth in subducting slabs, the response to tectonically imposed stresses deep in slabs should be ductile flow rather than abrupt seismic failure. Nevertheless, deep-focus earthquakes are common in slabs that descend far into the mantle.

The purpose of this research project is to explore the possible existence and structure (including composition, thermal, and stress) of a metastable olivine wedge in a subducting slab. For this we solve the two-dimensional, time-dependent heat conduction equation in a descending slab with the transformation of olivine to spinel controlled by temperature-dependent reaction kinetics. Both the latent heat of phase transformation and heat conduction parallel to slab dip are taken into account. The temperatures and olivine-spinel compositions are then used in a state-of-the-art material model to predict the stress fields around the metastable olivine wedge. The presence of the wedge and the accompanying stress field caused by the phase transformations has been hypothesized as the cause of deep-focus earthquakes. The ability to solve this complex problem is greatly enhanced by our collaboration, which combines expertise in geophysics, two-phase material behavior, and numerical modeling.

A paper on the thermal structure of a metastable olivine wedge in a descending slab was published in the *Journal of Geophysical Research.* Using the thermal structure, we completed new calculations on the nature of the stress field around a metastable olivine wedge. We have submitted these calculations in a second paper to the journal. The calculations add corroboration to the hypothesis that transformational stresses in subducting slabs cause deep-focus earthquakes.

Background

Deep earthquakes occur along inclined planes termed Wadati-Benioff zones, which extend down into the earth's mantle from below ocean trenches to depths approaching 700 km. Plate tectonics explains Wadati-Benioff zones as occurring within subduction zones where cold oceanic crust and lithosphere sink (or subduction) into the mantle as the descending limb of the cold thermal boundary layer of mantle convection. The frequency of earthquakes in subduction zones decreases exponentially with depth down to about 300 km; then the frequency increases again between 400 and 600 km before dropping off abruptly between 600 and 680 km.[1] This general pattern, a minimum in seismicity separating intermediate and deep earthquakes, is observed in all subduction zones with deep seismicity although the depth of the minimum varies slightly from zone to zone.

The cause of deep-focus earthquakes is a major puzzle in geodynamics because at great depth rocks should flow rather than break to relieve stress. In general, failure can occur by either brittle fracture or ductile flow. Fracture and frictional sliding are strongly inhibited by pressure, but not by temperature, because they involve the opening of tensile microcracks. The stress at which rocks flow, on the other hand, is strongly reduced by increasing temperature but is essentially unaffected by pressure, because motion of crystal dislocations is thermally activated. Thus, because temperature and pressure increase with depth in subducting slabs, the response to tectonically imposed stresses deep in slabs should be ductile flow rather than abrupt seismic failure. Nevertheless, deep-focus earthquakes are common in slabs that descend far into the mantle. The largest deep earthquake on record ($M_w = 8.3$), as well as the largest earthquake of any kind, deep or shallow, during the past 17 years, occurred 650 km beneath Bolivia on June 9, 1994. It was felt over broad regions of North America, and the many high-quality seismic records of this event and of the large Tongan earthquake of March 9, 1994 ($M_w = 7.6$), have spurred further interest in understanding the cause of deep earthquakes.

A number of mechanisms have been suggested to explain seismic failure deep in the mantle:
(a) thermal runaway instabilities,[2,3]
(b) transformation-induced faulting during the conversion of metastable olivine to spinel,[4–6]
(c) dehydration of hydrous minerals,[7] and
(d) reactivating of faults formed when the lithosphere was at the surface.[8] A proper evaluation of these potential causes of deep earthquakes requires detailed understanding of the deformation, state of stress, and temperature in subducting slabs, an understanding that can only be obtained through the combination of seismic observations and geodynamical modeling of the slabs.

Geodynamical modeling of the behavior of a subducting slab, including temperature effects and phase-transformation-induced stress effects, is the thrust of this research project.

Progress

We have developed a thermal model of a descending slab in which the transformation of olivine to spinel is controlled by pressure and temperature-dependent reaction kinetics. Two different formulations of the kinetics were considered with the main discriminant being the temperature range over which olivine converts to spinel at pressures of about 15 GPa (about 500°C to 515°C and 560°C to 650°C). We used a finite-element method to solve the coupled heat-conduction (perpendicular and parallel to the dip of the slab) and kinetics equations, and we included the latent heat of the phase transformation. Latent-heat release together with heat conduction parallel to the dip of the slab reduces significantly the length of the metastable olivine wedge and results in a very thin ($\leq\sim 5$ km) two-phase region. We employed the thermal parameter $v\tau\sin\delta$ (v is the velocity of the descending slab, τ is the age of the slab, and δ is the dip of the slab to the horizontal) to interpret the results for the length of the metastable wedge. For values of the thermal parameter smaller than about 4000 and 7000 km, depending on the model of the kinetics, no metastable olivine wedge exists (the critical value of 7000 km for the thermal parameter corresponds to the kinetics model with the lowest transition temperature range). The length of the metastable olivine wedge was also found to be very sensitive to the model of the kinetics and to the effects of adiabatic heating. If the occurrence of deep earthquakes is related to the transformation of metastable olivine to spinel, then data on earthquake depth[1,6] versus thermal parameter require that the onset of the reaction take place at temperatures of about 550°C to 575°C. In this case, the slab thermal parameter must be larger than 10,000 km for the metastable olivine wedge to extend down to 660 km. But deep earthquakes occur near 660-km depth in slabs with thermal parameter as small as about 5000 km (South America, for example). Either some deep earthquakes are unrelated to olivine metastability, or our knowledge of olivine-spinel reaction kinetics is incomplete.

Using the thermal and compositional structure computed as described above, in the past year we completed calculations of the stress field around the metastable olivine wedge. The calculational approach uses the state variable method[9] and a material model for olivine-spinel mixtures that we have appended to the ABAQUS code.[10] In particular, we examined the internal thermal and transformational stresses and their relationship to stresses caused by buoyancy forces.

These calculations showed that the stresses, particularly the differential stresses due to buoyancy, are negligible compared with the internal stresses that are due to the olivine-spinel transformation strain. Finer grids and more realistic creep laws do not change the dominance of the internal stresses over the buoyancy stresses, although the location and magnitude of the stress are affected. A zone of very high differential stress (~1.5 GPa) coincides with the olivine-spinel phase boundary. The width of this zone depends on the creep law used for spinel. Down-dip tensile stresses are found in the spinel region, along the olivine-spinel phase boundary. Down-dip compressive stresses are found inside the metastable olivine wedge.

If, as other investigators have done,[11,12] we assume that failure of spinel can be related to the differential stress, then our model predicts large earthquakes along the boundary of the metastable olivine wedge, at depths where deep-focus earthquakes occur. And finally, our computed principal stresses agree with seismic observations of deep focus earthquakes, which have down-dip compressional focal mechanisms.[6]

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Studies on Changes in HIV within and between Patients

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Abstract

Over the past year research at UC Irvine nearly completed the development and computer implementation of our algorithm for representing mutational relationships among DNA sequences. The program has reached the point where it works on simple test data sets and has been implemented in the Java programming language, which has the advantage of rapid development and ability to run on many kinds of computers.

This algorithm can be considered in two sections: the construction of a complex graph, and the reduction of that graph into simpler representations such as trees.

Construction of the Graph. The input for the algorithm is a sequence alignment containing multiple sequences. An alignment consists of sequences arranged such that corresponding nucleotide positions are thought to share common ancestry and that different states (A, C, G, and T) are originated by mutation of the sequence. In reconstructing descent relationships from genetic data, it is common to make the assumption of parsimony, which favors hypotheses requiring the minimal number of mutations. For standard evolutionary methods based on simple trees, the most parsimonious interpretation typically requires that some nucleotide positions will have mutated more than the minimal number of times required by the number of states observed. This is so because different patterns of variation at a position will fit some trees parsimoniously but not others, and rarely will all positions fit the same tree perfectly. Conversely, many different trees will have cumulative fits that are numerically equivalent by the parsimony criterion.

The first goal of our method is to construct a graph that contains all connections among the sequences (each connection being a hypothetically ancestor-descendent relationship) that are found in at least one of the most parsimonious trees. This graph will typically contain more connections than any single tree, and therefore it will not itself be a tree, but a more complex cyclic graph (network). It will provide a visual summary of the collection of all most parsimonious trees while being far more rapid to calculate than explicitly searching for those trees using standard methods. As a summary, this graph will have advantages over the consensus trees commonly used for this purpose. Consensus trees can contain groupings not found in any of the trees that they purport to summarize. Another difference is that our graph will visually convey the complexity of the underlying set of trees, whereas consensus trees in fact become simpler (less resolved) as the underlying trees become more diverse. Barring recombination, deviations from a simple tree structure in our graphs signal the presence of parallel mutations (homoplasy).

Beyond their use as summaries of multiple equally parsimonious trees, our graphs provide an avenue toward interpreting different regions of the sequences as the product of different genealogical histories. Recombination is a process by which a single sequence can inherit variation along two or more descent trees. HIV is certainly affected by recombination, so this is of some interest. In Figs. 1 and 2, any cycle can be interpreted as a potential instance of recombination, though many are likely due simply to parallel mutation. In the future we hope to take recombination analysis beyond the level of visual interpretation of cyclic graphs and provide numerical optimality measures of recombination versus parallel mutation as alternative hypotheses.

One example of such a complex tree is a mother and her infected infant (Fig. 1). In many such cases, we see a clustering of sequences found in the mother (labels beginning with M) separate from sequences found in infants (labels beginning with I). In the case shown, mother sequences are found on two sides of the infant cluster, suggesting multiple infecting virions or considerable homoplasy or recombination. These plots provide a visually intuitive taking-off point for searching for more focused tree analyses, which brings us to the second part of our method.

Reduction of the Graph. The cyclic graphs that are constructed by our algorithm are instructive in their own right, but they can also serve as the first step in the generation of simpler descriptions. For example, one can cut one edge (link) in a cycle and still have a connected, though simpler, graph. In a planar graph, one can identify nonoverlapping cycles and then remove one edge from every cycle in such a way that the resulting simplified graph becomes a tree. This can be generalized to nonplanar graphs as well. We have developed an algorithm for identifying a set of cycles in a graph and breaking these cycles in such a way that the result is guaranteed to be a most parsimonious tree. Further, once we have created the data structure required to find the first most parsimonious tree, we can traverse this structure and find all other most parsimonious trees. Figure 2 is an example of a 16-cycle planar graph constructed from a small artificial data set of 13 sequences and 24 of the 47 shortest trees of length 22 found by the cycle-breaking algorithm.

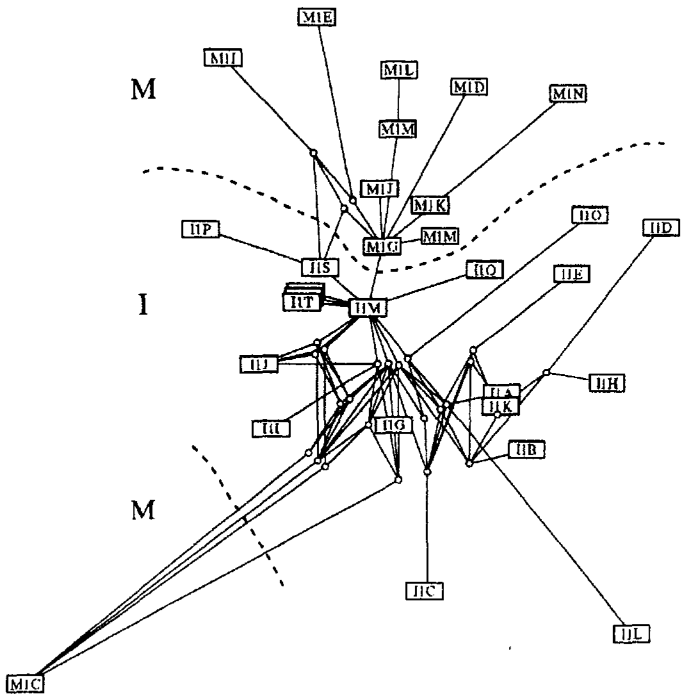

Fig. 1. HIV sequence network for mother and infant isolates.

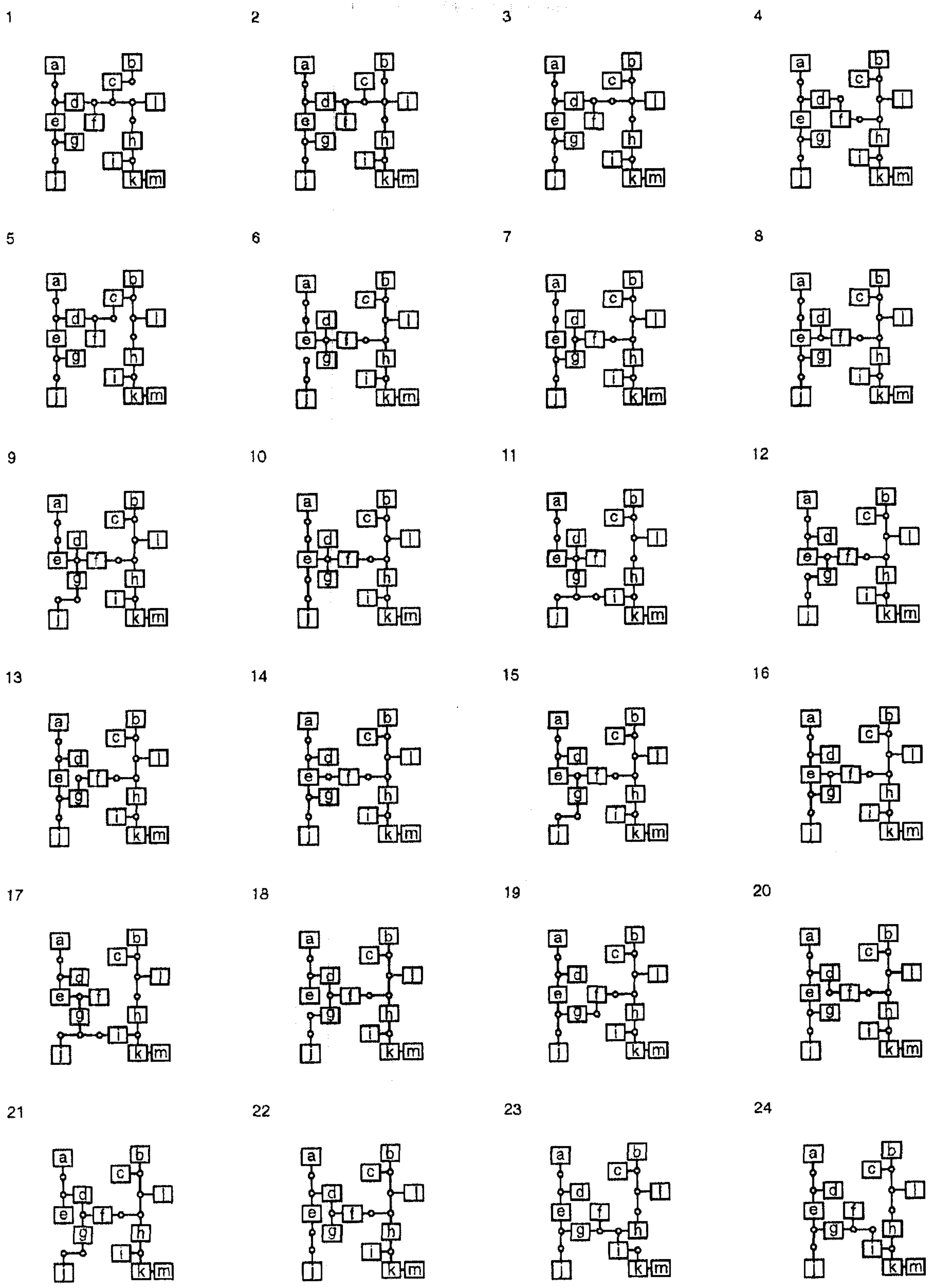

Fig. 2. Twenty-four of 47 equally most parsimonious trees.

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Metal-Insulator Transitions in Strongly Correlated Electronic Materials

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Abstract

Novel electronic materials play an ever increasing role in modern technology. Understanding how strong electronic correlations lead to novel material properties is important in the development of devices, as well as in improving our understanding of the basic physics of these phenomena. Our collaboration combines theoretical and experimental studies of materials that are at the forefront of current research.

Colossal magnetoresistance materials have the potential of increasing the magnetic storage of information by a hundredfold. Ferromagnetic spin interactions between itinerant and localized electrons, as well as electron phonon coupling, are thought to be important components in understanding these materials. Experimentally, we have measured the x-ray absorption fine structure of $La_{1-x}Ca_xMnO_3$. We find that lattice distortions, characteristic of slow polarons, occur in the high-temperature (insulating) state but are greatly reduced in the low-temperature (metallic) state. Theoretically, we have found that the double exchange model, which is thought to describe the spin interactions, has a richer phase diagram than expected. We also predict that in the strong coupling regime of this model, anomalous persistent currents should occur when small rings are placed in a magnetic field. We have also developed a new technique to calculate the ground state, excited state, and properties far from equilibrium for an electron coupled to phonons (the same coupling that appears in colossal magnetoresistance materials). The ground state energy is calculated 10 million times more accurately than any previously published results.

Electronic devices often involve heavily doped semiconductors and thin metal films. These are disordered systems in which the electrons interact via Coulomb interactions. Typically, we expect electrons to respond rapidly to perturbations. However, we have shown that electrons in such disordered systems can hop extremely slowly in agreement with conductance measurements.

The technological applications of high-temperature superconductors, require

that there be no loss or dissipation. The primary source of resistance and dissipation in these superconductors is the motion of vortices. A vortex is a filament of magnetic flux. One way to prevent vortex motion is to inhibit melting of the vortex lattice. We have proposed a novel mechanism in which vortex lattice melting is induced by defects consisting of interstitial vortex lines and vacancies.

$BaVS_3$ is a metal at high temperature and an insulator at low temperature. In an effort to better understand this metal-insulator (MI) transition in $BaVS_3$, we have measured the Hall Effect, which shows evidence for precursive insulating behavior in the metallic state. Our measurements of the magnetization and magnetoresistance shows that the application of large (20- to 45-tesla) magnetic fields has only a very weak effect on the MI transition. This rules out models where the spin correlations play a strong role and suggests that the MI transition may involve the onset of a charge density wave. We have also characterized the structure and electronic and magnetic behavior of a related compound, $NaBaVS_4$.

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9804

Three-Dimensional Models of Crustal Deformation along the San Andreas Fault System

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Abstract

Large earthquakes represent the most significant natural hazard to the state of California. To better understand the physical processes of the earthquake cycle, we are engaged in a collaborative research effort involving scientists at Los Alamos National Laboratory and the University of California. This research focuses on two major topics: (a) evaluating models of the fundamental architecture of the San Andreas Fault system at depth and (b) evaluating models of the physical processes involved in the mechanical interaction of individual faults, with a focus on the effects of postseismic processes on the loading of neighboring faults. These topics are crucial for gaining

a better understanding of earthquake processes related to interseismic stress buildup and the redistribution of stress, which occurs after an earthquake.

We have approached these objectives by combining both analytical and numerical approaches for calculating the response of coupled elastic-viscoelastic Earth models to crustal loading under varied boundary conditions. We use an analytic code previously developed by Pollitz, designed for the gravitational-viscoelastic response of horizontally layered Earth models to stress changes following earthquakes. In addition, we use a commercial finite element (FE) code (SPECTRUM), which computes time-dependent deformation of three-dimensional viscoelastic models with embedded faults using either source boundary conditions (i.e., stress changes induced by an earthquake) or edge boundary conditions which simulate the large-scale tectonic velocity accommodated across the San Andreas Fault system. This year we have made considerable progress using both of these computational tools.

From consideration of stress propagation through oceanic lithosphere, we found that 5% transient fluctuations in background relative plate velocity off California may have occurred in the 1980s and early 1990s, suggesting a major role for external triggering of the many California earthquakes with magni- tudes of 5 or greater, which occurred during that time period. Preliminary FE modeling of possible small changes in the imposed boundary conditions of plate interaction indicate that stress changes capable of generating earthquakes may be produced in the lower part of the seismo- genic layer and that the time scale of the external perturbation relative to the relax-ation time of ductile material beneath California plays an important role in generating sufficiently high transient stresses.

Work done in the first year and earlier this year to implement frictional elements in the FE algorithm is now reaching fruition. Using SPECTRUM, we have investigated spatiotemporal patterns of earthquake occurrence on a single fault subjected to velocity boundary conditions (simulating relative plate motion), allowing for both steady, increasing loading on the fault and the stress changes accompanying the coseismic rupture of fault patches and their subsequent relaxation with time. A Coulomb failure criterion is prescribed from an initial state in order to control the behavior of the fault. Our results indicate that patterns of stress concentration in the upper crust depend to a large extent on the width of ductile shear zones occupying the uppermost mantle beneath an active fault.

The main parameters that control lithospheric stress diffusion are the viscosity of the lower crust and upper mantle. In two separate studies, one in northern California (Pollitz, Bürgmann, and Segall 1998) and one in southern California (Pollitz, Peltzer, and Bürgmann 1998), we have interpreted geodetic data and estimated these parameters. Our results suggest a generally ductile lower crust, a relatively strong uppermost mantle beneath part of northern California, and a relatively weak uppermost mantle beneath the central Mojave Desert.

SPECTRUM has been run on the SGI-Challenge at UC Davis on somewhat less ambitious problems (which require less space and computation time) than eventual models using multiple faults and a realistic three-dimensional rheology which we intend to implement on Los Alamos supercomputers in our third year.

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9806

First Principle Studies of the Molecular Mechanism for Protein Folding Funnels

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Abstract

Proteins comprise the machinery that controls most of the functions in living organisms. The fact that their activity depends on their three-dimensional structure and dynamics and not simply on their amino-acid sequence presents novel conceptual challenges.
Biology, however, has been able to connect these two apparently distinct properties. Scientists have been amazed by the fact that proteins are able to fold into the required structure spontaneously. This property has led to the belief that all the information necessary to achieve folding is contained in the sequence, at least for small globular proteins. How are these molecules able to accomplish this

task? Our research efforts focus on how new theoretical approaches supported by experimental results have created a framework able to differentiate foldable from nonfoldable sequences.

By working with different representations of protein-like heteropolymers, varying all the way from lattice to all-atom representations, we have been identifying the main features that differentiate a typical or random heteropolymer from the ones that are able to fold into a well-defined structure (protein-like). In particular, we have been exploring the interplay between two of these features: energetics and topology. Energetic frustration can be reduced with the appropriate design for the protein sequence. Topological frustration is more complicated because it is a consequence of the polymeric nature of the chain and the shape of the folding motif. Some choices of the folded structure may be easier to design sequences that fold to them than for other folds. In the extreme case in which we choose to have very asymmetric fold motifs, it may be practically impossible to design sequences that fold to them. Until now, most computational studies of protein folding have been performed for only a few protein motifs, using only a few types of minimalist model. Further studies for a larger number of protein motifs and using different representations for the proteins are necessary before we will be convinced that a full quantitative and general understanding of the this question has been obtained.

Using this theoretical framework, we have been able to establish a strong connection to the experimental data of the Oas' group at Duke University. Recent experimental and theoretical developments have shown that although the ensemble of transition states for small fast-folding proteins is delocalized over the entire protein structure, there is a certain degree of inhomogeneity; that is, some regions of the protein have more native structure than other regions in this transition region. These experiments show evidence which strongly indicates that, for these small proteins, a dominant part of this variation in native structure is created by topological factors, such as polymeric constraints of the protein chain and the shape of the native fold, rather than energetic factors, such as differences in the strength of residue/residue interactions. To demonstrate this, we show that an off-lattice minimalist model of (a thermostable variant of) the lambda 6-85 protein, in which the native topology is retained but the energetic frustration is substantially reduced, has a transition state that is similar (accounts for most of the variation) to the one experimentally determined for the lambda 6-85 protein.

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Onuchic, J.N., "Exploring the Protein Folding Funnel Landscape: Connecting Theory and Experiments," Michigan Institute of Technology, Houghton, MI, October 1998 (invited).

Onuchic, J.N., "Exploring the Protein Folding Funnel Landscape: Connection between Theory and Experiments," Department of Biochemistry, Duke University, Durham, NC, October 1998 (invited).

Onuchic, J.N., "Exploring the Protein Folding Funnel Landscape: Towards a Connection between Theory and Experiments," Johns Hopkins University, Baltimore, MD, April 1998 (invited).

Onuchic, J.N., "Navigating the Protein Folding Funnel Landscape," Washington State University, Pullman, WA, October 1998 (invited).

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Onuchic, J.N., "Theoretical and Computational Aspects of Protein Foldind," Doing Science at the Interface Workshop, Burroughs Welcome Fund, Berkeley, CA, June 1998 (invited).

Onuchic, J.N., "What Are the Constraints on the Evolution and Diversity of Bioplymers," Dahkem Workshop on Simplicity and Complexity in Proteins and Nucleic Acids, Berlin, Germany, May 1998 (invited).

9808

Atmospheric-Pressure Plasma Jet Cleaning of Semiconductor Materials

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Abstract

The atmospheric-pressure plasma jet is an exciting new technology that may be applied to the "pollution-free" cleaning of semiconductor wafers and to the decontamination of transuranic wastes. An environmentally acceptable replacement for wet solvent cleaning is of considerable importance to the Department of Energy, because in nuclear weapons production these latter cleaning methods generate mixed chemical and radioactive wastes that are no longer allowed under federal regulations. This work is also important to the University of California because the California economy relies to a great extent on the semiconductor industry and because this industry is under pressure to reduce waste production. The atmospheric-pressure plasma

jet employs benign gases, such as helium and oxygen, to produce reactive intermediates that attack and clean surfaces. Thus far, we have demonstrated that the plasma jet can etch organic compounds, tantalum (a plutonium surrogate), and other materials at rapid rates near room temperature. A $CF_4/O_2/He$ plasma jet removes tantalum at 6.0 µm/min, which is nearly an order of magnitude faster than reported with conventional low-pressure plasmas.

Our focus this year was to accurately predict the physical properties of the plasma jet by using experimental and theoretical methods. In the latter case, a reactive flow model was developed to simulate the reactions of the activated species in the effluent of an O_2/He plasma. Experimental measurements of the concentrations of ozone and singlet sigma metastable oxygen were made using ultraviolet absorption and visible emission spectroscopies. These results were input into our kinetic model, so that we could then predict the concentrations of singlet delta metastable oxygen and oxygen atoms. We were very excited to learn that the plasma jet produces very high concentrations of ground-state oxygen atoms, on the order of 1×10^{16} cm^{-3} (or about 400 ppm), at close to room temperature. These oxygen atoms are most likely responsible for oxidizing and removing organic contaminants from silicon wafer surfaces. We have also investigated the ion and electron dynamics in the plasma with the aid of a one-dimensional transport model. This model revealed that the plasma is weakly ionized and not at thermal equilibrium. The electron density and electron temperature were estimated to be 10^{10}–10^{11} cm^{-3} and 3–4 eV, respectively. Work continues on the development of this important new environmentally benign decontamination and cleaning technology.

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Nonrefereed Publication

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Selwyn, G.S., I. Henins, J. Velarde, J.Y. Jeong, S.E. Babayan, and R.F. Hicks, "Contamination Control for Future Device Processing: Good Vibrations to Plasma Jets," Meeting of the American Institute of Chemical Engineers, Los Angeles, CA, November 17, 1997 (contributed).

Patent

S.E. Babayan, R.F. Hicks, and G.S. Selwyn, "Large Area Atmospheric-Pressure Plasma Jet," U.S. patent application in preparation.

9809
Strategies for Delivering the Radiation Sensitizer Nitric Oxide in Cancer Treatment

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Abstract

This year we were concerned with the use of flash photolysis apparatus at Los Alamos to study reactive intermediates formed by the photo-excitation of metal nitrosyl and nitrito complexes. These compounds are models for therapeutic drugs which may deliver nitric oxide (NO), a sensitizer for radiation cell-killing, to tumor tissues upon photoreaction. The time resolved spectroscopic results have aided in designing different drugs and new strategies for NO delivery for applications in cancer chemotherapy. Based in part upon the successful studies to date, a new generation of NO-releasing compounds has been prepared at UC Santa Barbara, and these are the subject of the continuing research. Several manuscripts acknowledging the support of this CULAR grant are listed below.

At UC Santa Barbara we have researched the synthesis of new metal nitrosyl complexes and photochemical studies using time-resolved optical and (single frequency) time-resolved infrared (TRIR) spectroscopy. At Los Alamos we have concentrated on the use of the stepped-scan Fourier transform infrared instrumentation to obtain temporal changes in the infrared spectra over a range of frequencies not easily accessible in the point-by-point mode with single-frequency detection. The systems investigated include the Roussin's black and red salt anions $Fe_4S_3(NO)_7^-$ and $Fe_2S_2(NO)_4^{2-}$, the several ruthenium porphyrins complexes Ru(P)(NO)(ONO) (ms 2 and 3), and the hydrocarbon activation photocatalyst $Rh(Me_3P)_2(CO)Cl$ (ms 1), which is closely related to rhodium nitrosyl complexes having potential as precursors for NO delivery. The iron and ruthenium compounds each have potential applications in mammalian biology. For example, the red salt anion has already been shown to be an effective photolysis-triggered sensitizer of radiation cell-killing, although in the absence of light, this complex ion may have protective effects for normal cells. Aspects of these results were reported in talks at several national and international meetings listed below.

Collaborative TRIR studies of the hydroformylation catalyst $HCo(CO)_3(PPh_3)$ were also carried out by UC Santa Barbara personnel visiting Los Alamos, and aspects of this work were reported by Peter Ford at the Fourth DOE/BES Conference on Homogeneous Catalysis and Organometallic Chemistry in Baltimore (June 1998). In addition, three UC Santa Barbara graduate students so far have included data accumulated as part of these collaborative studies in their Ph.D. theses (Brian Lee, July 1997; Jim Bourassa, February 1998; and Jon Bridgewater, September 1998).

Another major accomplishment has been an effective working relationship between the UC Santa Barbara and Los Alamos groups to carry out measurements on the step-scan TRIR system at Los Alamos (and complementary synthesis and photochemical studies at UC Santa Barbara) to demonstrate the feasibility of proposed experiments, to determine modifications of the respective systems needed to bring the proposed collaborative research to fruition, to put these into action and to report these results at meetings and in publications.

Refereed Publications

Bridgewater, Jon S., Brian Lee, Stefan Bernard, Jon R. Schoonover, and Peter C. Ford, "Time Resolved Infrared Spectral Studies of Photochemically Induced Oxidative Addition of Benzene to trans-$RhCl(CO)(PMe_3)_2$," *Organometallics* 16, 5592 (1997).

Lorkovic, Ivan M., Katrina M. Miranda, Brian Lee, Stefan Bernhard, Jon R. Schoonover, and Peter C. Ford, "Flash Photolysis Studies of the Ruthenium(II) Porphyrins Ru(P)(NO)(ONO). Multiple Pathways Involving Reactions of Intermediates with Nitric Oxide," *J. Am. Chem. Soc.* **120**, 11674 (1998).

Ford, P.C., J. Bourassa, K. Miranda, B. Lee, I. Lorkovic, S. Boggs, S. Kudo, and L. Laverman, "Photochemistry of Metal Nitrosyl Complexes. Delivery of Nitric Oxide of Biological Targets," *Coord. Chem. Rev.* 171, 185 (1998).

Bourassa, James, Brian Lee, Stefan Bernard, Jon Schoonover, and Peter C. Ford, "Flash Photolysis Studies of Roussin's Black Salt Anion: $Fe_4S_3(NO)_7^-$" (submitted to *Inorg. Chem.*).

Presentations

Ford, Peter C., "Flash Photolysis Studies of Iron Nitrosyl Complexes. Mechanisms of NO Reactions with Biological Relevant Metal Centers," Symposium on Biological Chemistry and Cellular Targets of Nitric Oxide, Graz, Austria, August 1998 (invited).

Ford, Peter C., "Kinetics and Mechanisms of Nitric Oxide Reactions with Metal Centers and Other Biologically Relevant Targets," Meeting of the American Chemical Society, Dallas, TX, April 1998 (invited).

Ford, Peter C., "Mechanism Studies in Nitric Oxide Chemistry," *I Workshop Brasileiro: Propriedades e Aplicações de Oxido Nitrico e Correlatos*, Ribeirão Prêto, Brazil, November 1998 (invited).

Ford, Peter C., "Mechanistic Studies of the Reactions of Nitric Oxide Involving Metal Centers," Second RIKEN International Symposium on Nitric Oxide Chemistry in Biology, Wako-shi, Japan, December 1998 (invited).

9810
Microbially Mediated Dissolution of Iron Oxides

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Abstract

Iron oxides from the surface "A" horizon of an Oxisol from Brazil were characterized by using advanced microscopic imaging techniques. Petrographic light microscopy allowed bulk characterization of the soil and location of runiquartz where iron oxides had concentrated. Scanning electron microscopy (SEM) was found not to be useful in characterizing iron oxides from the soil unless mineral separation procedures were used. Iron oxides were in too low abundance (~5%) and too similar in shape and size to highly weathered kaolinite to be differentiated easily by SEM.

Transmission electron microscopy (TEM) of ultrathin sections and colloidal fractions of the soil gave the most useful results. Iron oxides from the Oxisol were predominantly goethite, poorly crystalline, subrounded in shape, and mostly <60 nm in diameter. They were distributed randomly in the soil fabric, but often associated with kaolinite minerals and with decaying organic residues. Atomic force microscopy gave similar results in morphology for goethite to what was found by TEM.

Tapping-mode atomic force microscopy imaging yielded significantly fewer artifacts in imaging soil iron oxides than other modes. The soil goethite corresponded closely in size to crystalline synthetic aluminum-substituted goethite. The shape of the goethite was similar to aluminum-substituted goethite produced from oxidation of Fe(III) solutions at room temperature, but with much larger crystal size. Weak edge pitting dissolution features in the soil samples of goethite correspond to cavernous dissolution of synthetic aluminum-substituted goethite.

Nonrefereed Publication

Vrdoljak, G.A., "Ultramicroscopy of a Brazilian Oxisol," Ph.D. Thesis, University of California at Berkeley (1998).

Presentations

Vrdoljak, G.A., and G. Sposito, "Investigations of Aggregate Hierarchy in a Brazilian Oxisol," Meeting of American Society of Agronomy, Crop Science Society of America, Anaheim, CA, October 1997 (contributed).

Vrdoljak, G.A., and G. Sposito, "Organic-Mineral Association in a Tropical Soil" Meeting of the American Chemical Society, Division of Environmental Chemistry, Anaheim, CA, March 21–25, 1999 (contributed).

9811

An Innovative Numerical Model for the Simulation of Advanced Droplet-Based Materials Processes

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Abstract

The technological potential and the importance of spray and droplet-based manufacturing techniques to the development of advanced rapid prototyping and near net-shape manufacturing processes is indisputable. This research program combines the complementary expertise at UC Irvine and Los Alamos to develop an innovative numerical simulation tool that can be used to both further our current understanding of spray and droplet-based manufacturing processes and optimize such processes by providing a genuine, quantitative predictive capability. This new numerical tool is based on the computer codes RIPPLE and TELLURIDE, the first developed at Los Alamos several years ago and the second under development at Los Alamos. Thermal energy solvers, as well as nucleation and rapid solidification concepts and numerical models being developed at UC Irvine, are being incorporated into these programs. The numerical tool being developed will in itself be a significant outcome as it is a step toward the development of a "virtual manufacturing" capability where designs can be optimized without actually fabricating them, thus significantly cutting development costs.

Developments during the past year include a model to predict the characteristics of materials processed using reactive spray atomization and deposition. The materials considered are aluminum alloys while target dispersoids are primarily oxides. These may be obtained by the reaction of oxygen-containing atomization gas mixtures with molten alloy droplets. Droplet position and velocity histories are obtained from the numerical solution of the one-dimensional equation of motion. The energy equation inside the droplet is solved numerically using finite-differences to predict the spatially resolved temperature field. The solid/liquid interface progression rate is estimated using a power law while an oxidation rate expression based on the Mott-Cabrera theory is used for the oxide thickness. Such a model should prove very valuable in determining the parameters controlling the volume fraction and the size distribution of the dispersoids for various systems.

In addition, porosity formation in spray deposition processes was investigated. The emphasis is on one possible mechanism of micropore formation during droplet spreading and solidification: liquid-jet overflow. The results obtained allow a detailed description of the liquid-jet overflow mechanism and of the resulting solidified disk morphology.

Finally, a numerical solution of the thermal energy equation based on the enthalpy method was developed and incorporated into RIPPLE. The calculation domain includes both the deforming droplet and the substrate. Numerical tests were performed for the solidification of droplets impinging on flat substrates. The droplet/substrate combinations

included water on ice, titanium on titanium, aluminum on quartz, and water on aluminum.

Refereed Publications

Delplanque, J.-P., and R.H. Rangel, "A Comparison of Models, Numerical Simulation, and Experimental Results in Droplet Deposition Processes," *Acta Materialia* 46, 4925 (1998).

Delplanque, J.-P., and R.H. Rangel, "Simulation of Liquid Jet Overflow in Droplet Deposition Processes" (submitted to *Acta Materialia*).

Rangel, R.H., and X. Bian, "Undercooling and Contact Resistance in Stagnation-Flow Solidification on a Semi-infinite Substrate," *Int. J. Heat Mass Transfer* 41, 1645 (1998).

Presentations

Canton, A., J.-P. Delplanque, and R.H. Rangel, "Heat Transfer and Solidification Model for a Droplet Impinging on a Solid Substrate," American Society of Mechanical Engineers, International Mechanical Engineering Congress and Exposition, Anaheim, CA, November 1998 (contributed).

Rangel, R.H., "Metal Droplet Deposition Modeling for Manufacturing Applications," Department of Chemical and Metallurgical Engineering, University of Barcelona, Spain, December 1997 (invited).

9813

Nanosecond Time-Resolved Circular Dichroism Spectroscopy of Temperature-Jump Initiated Protein Folding Dynamics

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Abstract

This project is a feasibility study aimed at the development of a new type of time-resolved circular dichroism (TRCD) instrument combining fast, ellipsometric detection of circular dichroism and the fast initiation of protein folding by a rapid jump in temperature. Unlike conventional circular dichroism instruments, which measure the difference in the relative amounts of left- and right-hand circularly polarized light transmitted by a sample, an ellipsometric instrument measures the relative increase in the ellipticity of a nearly linearly polarized light beam, a far more sensitive approach to measuring circular dichroism. The temperature jump (T-jump) is provided by the rapid deposition of heat into the water solvent upon absorption of a brief pulse of

infrared laser light. The new instrument will have five orders of magnitude superior time resolution compared with conventional instruments and thus will solve a great many measurement problems encountered by biophysicists today. In particular, it will allow us to view early events during the folding of proteins to their native three-dimensional structures.

Protein folding is one of the great unsolved problems of modern molecular biology. Biologically, a protein only functions in its folded, or native, state and it only folds to a specific geometry coded in its amino acid sequence. An unanswered question concerns how quickly a protein molecule changes from a random coil to an organized structure. That is, at what time does secondary structure begin to appear in the folding process? Conventional approaches to circular dichroism measurements of protein folding lack the time resolution necessary to detect early steps in folding, which are expected to occur on the nanosecond to microsecond time scale. By demonstrating the feasibility of combining a novel ellipsometric technique for nanosecond TRCD spectroscopy and T-jump initiation of folding, we are developing an instrument capable of obtaining the data needed to answer such fundamental questions.

The notable accomplishment toward the goal of nanosecond T-jump TRCD measurements during the third year was the development of an improved laser T-jump source. We built an optical parametric oscillator (OPO) system generating intense infrared light pulses at 1.5 µm for T-jumps (about 10° in aqueous sample volumes of 0.05 mm^3) that are larger and more stable than those we could obtain from our previous source, a Raman shifter. Our operating experience with this system over the last year allowed us to identify the quality of the mode structure in the Nd:YAG laser pumping the OPO as the single most important parameter limiting the reliability of this T-jump source for future experiments. Upgrading the mode quality should lengthen the mean time between OPO crystal failures sufficiently to permit nanosecond T-jump measurements of time-resolved optical rotatory dispersion (TRORD) in proteins such as myoglobin. TRORD is closely related to TRCD, the ultimate goal of this project (optical rotary dispersion and circular dichroism are interconverted by use of Kramers-Kronig transforms), but is much less susceptible to artifacts, particularly the artifact from cell window strain birefringence created by the shock wave from the T-jumped solvent.

Refereed Publications

Chen, E., R.A. Goldbeck, and D.S. Kliger, "Nanosecond Time-Resolved Polarization Spectroscopy Applied to Protein Folding," in *Laser Techniques for Condensed-Phase and Biological Systems*, N.F. Scherer and J.M. Hicks, Eds. (SPIE, Bellingham, WA, 1998), Vol. 3273, pp. 68–79.

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Goldbeck, R.A., D.B. Kim-Shapiro, and D.S. Kliger, "Fast Natural and Magnetic Circular Dichroism Spectroscopy," *Annu. Rev. Phys. Chem.* 48, 453 (1997).

9814
Domain Wall Dynamics in Ferroelectric Materials

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Abstract

This was the second year of our joint experimental and theoretical collaboration on the nanoscale study of domain wall dynamics in ferroelectric materials. It has had a necessarily strong experimental focus. We have detected single domain walls in ferroelectric single crystals with 80-nm resolution using the near-field scanning optical microscope (NSOM). We have generated the first strain field distribution and strain energy measurement at the domain wall. These measured values have been supplied to Los Alamos for benchmarking newly developed continuum models of domain walls in ferroelectrics. In the coming year, we propose to investigate the mobility of domain walls under applied fields with the NSOM. Values of the pinning density and pinning energy and mobility will be supplied to Los Alamos for large-scale modeling of the dynamics. A more extensive discussion is provided in the body of the proposal. Ferroelectric materials provide unique solutions to many engineering problems and are used extensively in modern technology. Examples include
(a) transducers and actuators,
(b) ferroelectric memory elements,
(c) optical wave guides and switches,
(d) chemical sensors that use thin films of metal oxides, (e) pyroelectric infrared detectors, and (f) ultrasound imaging and microscopy. Domain wall movements have been conjectured to be responsible for over 50% of the energy losses in devices. Yet, we have an extremely limited understanding of the relationship between microstructure, mesoscopic domain structures, and the macroscopic dynamic response. Although there has been some recent theoretical progress (using phenomenological models 5), vital experimental information on single domain wall dynamics is required to enable key new theoretical advances. The lack of experimental data on domain wall nucleation, mobility, and annihilation has been a major obstacle to the development of a fully dynamic theory of domain wall dynamics.

We are using a polarization sensitive transmission mode and collection mode NSOM for the investigation of time-resolved submicron domain wall dynamics in ferroelectrics. The NSOM is a nondestructive optical probe with a spatial resolution of 50 nm and a temporal resolution of 30 femtoseconds. This will be the first measurement of the microdynamics of individual ferroelectric domain walls on a femtosecond time scale. This experiment will yield for the first time a value for the driving and restoring forces on the domain walls, the effective mass of the lattice, the pinning density, and the coupling of the domain walls to dissipative processes such as lattice vibration and dopant diffusion.

In the ferroelectric state the crystals are composed of many small domains, with each domain having a uniform polarization. The mechanical deformation accompanying the spontaneous polarization leads to substantial strain and related birefringence at domain boundaries. This leads to polarization rotation for reflected and transmitted light. A variety of experimental techniques such as polarizing optical microscopy, etching, colloidal decoration, the anomalous dispersion of x-rays, SFM and TEM have been used to study static domains. However, their applicability for the study of domain wall dynamics is limited because of either poor resolution or sample requirements.

Refereed Publications

Yang, T.J., and U. Mohideen, "Nanoscale Measurement of Ferroelectric Domain Wall Energy by Near-Field Scanning Optical Microscopy," *Phys. Lett. A* 250, 205 (1998).

Yang, T.J., U. Mohideen, V. Gopalan, and P. Swart, "Observation and Mobility Study of Single 180° Domain Walls Using a Near-Field Scanning Optical Microscope" (to be published in *Ferroelectrics*).

Nonrefereed Publications

Yang, T.J., and U. Mohideen, "Collection Mode Near-Field Scanning Optical Microscopy of Single Domain Walls," *Bull. Am. Phys. Soc.*, March meeting, Los Angeles, CA (1998).

Yang, T.J., and U. Mohideen, "Nanoscale Measurement of Ferroelectric Domain Wall Energy and Dynamics by Near-Field Scanning Optical Microscopy," *Bull. Am. Phys. Soc.*, March meeting, Los Angeles, CA (1998).

9816

Mechanism of Cell-Viral Membrane Fusion Induced by the Influenza Hemagglutinin

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Abstract

The overall aim of this project is to elucidate the molecular mechanism of the most crucial step in influenza virus infection: cellular-viral membrane fusion induced by influenza hemagglutinin (HA). The HA protein is a spike protein on the surface of the influenza virus responsible for cell recognition and for mediating the fusion of cellular and viral membranes, which allows the passage of the viral genome into the host cell. A thorough understanding of the role of HA in viral infection will eventually lead to the development of new antiviral drugs. It is believed that the fusion process proceeds in several sequential steps, and to understand this process it is necessary to identify and characterize fusion intermediates and to resolve in time the sequential protein conformational changes and the interaction with the membrane.

Recent structural studies from UC Berkeley have revealed that a structural motif, a triple-stranded coiled coil, plays essential roles in HA function. The key events in HA-induced membrane fusion

involve conformational changes in HA (formation and disruption of the coiled coil). This CULAR proposal focuses on understanding the energetics and dynamics of the coiled-coil structural motif. State-of-the-art Fourier transform infrared (FTIR) and time-resolved infrared (TRIR) techniques recently developed at Los Alamos are employed. These techniques are uniquely suited for testing some crucial aspects of these new ideas.

As a first step toward the understanding of the mechanism of HA and to gain valuable insights into the formation and the disruption of coiled coils, peptides based on the best-characterized GCN4 leucine zipper protein were synthesized and purified to yield samples suitable for high-quality infrared measurements. Temperature-unfolding FTIR experiments, performed at Los Alamos, revealed some unique signatures of coiled coils in infrared spectra. Most important, the temperature-jump experiments using the ultrafast TRIR technique revealed unprecedented two distinct phases in the unfolding process of the coiled coil. This new observation significantly differs from the current mechanistic model and will help us formulate a new concept in protein folding.

Refereed Publications

Epand, R.F., J.C. Macosko, C.J. Russell, Y.-K. Shin, and R.M. Epand, "The Ectodomain of Influenza Hemagglutinin Is Sufficient for Rapid Membrane Fusion" (to be published in *J. Mol. Biol.*).

Poirier, M.A., W. Xiao, J.C. Macosko, C. Chan, Y.-K. Shin, and M.K. Bennett, "The Synaptic SNARE Complex, a Parallel Four-Stranded Helical Bundle," *Nat. Struct. Biol.* 5, 765 (1998).

Russell, C.J., T.E. Thorgeirsson, and Y.-K. Shin, "The Membrane Affinities of the Aliphatic Amino-Acid Sidechains in an a-Helical Context Are Independent of Membrane Immersion Depth," *Biochemistry* 38, 337 (1999).

Russell, C.J., D.S. King, T.E. Thorgeirsson, and Y.-K. Shin, "De Novo Design of a Peptide Which Partitions between Water and Phospholipid Bilayers as a Monomeric a-Helix," *Protein Eng.* 11, 539 (1998).

Nonrefereed Publication

Shin, Y.-K, "K+ Channel Gating Mechanism Proposed Using EPR," *Nat. Struct. Biol.* 5, 418 (1998).

9819

Functionalized Fullerenes: Optimized Materials for Optical Limiting and Self-Assembly

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Abstract

In the past year, we have successfully completed the design and synthesis of the first water-soluble derivative of PPV (MSP-PPV), a compound with remarkable properties. This highly luminescent polymer is ideal for polyelectrolyte self-assembly, and we have demonstrated multilayer assemblies with arbitrary thickness, high quantum efficiency for emission, and controlled energy and charge transfer in a preferred direction. We have observed ultrafast charge transfer (300-fs time constant) in self-assembled films with water-soluble fullerenes developed earlier in this project. Together, these ionic molecular building blocks form the basis for a powerful new class of nonlinear optical materials and set the stage for a variety of applications, including sensors for proteins and organic compounds, solar cells, and holographic signal processing.

Publications

Chen, L., D. Whitten, D. McBranch, H.-L. Wang, R. Helgeson, and F. Wudl, "A New Flourescent Biosensor Based on a Water-Soluble Conjugated Polymer" (submitted to *Science*).

Wang, H.-L., D. McBranch, V. Klimov, R. Helgeson, and F. Wudl, "Controlled Unidirectional Energy Transfer in Conjugated Polymer Superlattices" (submitted to *Chem. Phys. Lett.*).

Presentation

Helgeson, R., P. Buchacher, Y. Yang, and D. McBranch, "Water-Soluble PPV for Organic Light-Emitting Devices," Meeting of the Materials Research Society, Boston, MA, November 30–December 4, 1998 (invited).

Patent

L. Chen, D. Whitten, D. McBranch, H.-L. Wang, R. Helgeson, and F. Wudl, "A New Flourescent Biosensor Based on a Water-Soluble Conjugated Polymer," U.S. patent applied for.

9820
The Development of Conjugated Polymer Membranes for Gas Separations

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Abstract

Separating pure components from mixtures is of great industrial importance. Our work is devoted to using novel conjugated polymers that can be modified after their synthesis to enhance their separating abilities toward gases, liquids, and enantiomers. Current gas separation technologies often suffer from high capital costs, poor energy efficiency, and generation of secondary pollution. In recent years, membrane-based separations have proven to be economically competitive with the currently used methods, while often possessing several advantages such as reduced energy costs and reductions in secondary pollution. For effective gas separations a membrane must combine high selectivity with high gas throughput. This combination of properties is being achieved with the conjugated polymer polyaniline. Polyaniline can be tailored through a doping process to give one of the most highly selective membranes for gases, although with modest permeability. To enable higher gas fluxes, Los Alamos National Laboratory is developing asymmetric hollow fiber membranes of polyaniline. In addition, polyaniline membranes capable of separating gases can also function as pervaporation membranes for separation of liquids. An understanding of the basic transport mechanisms involved in both liquid and gas separations is being pursued. Solvent systems for dissolving up to 25% polyaniline in its base forms have been developed at Los Alamos and have enabled us to produce integrally skinned asymmetric membranes. The "thin-skin" asymmetric structure enables a three to four order of magnitude increase in gas throughput relative to previously studied dense films.

Los Alamos has filed for patents relating to the preparation of polyaniline flat sheet and hollow fiber membranes for gas separation applications. This work is a significant accomplishment that may enable commercial realization of the highly selective separation phenomenon, which we jointly discovered using thick dense films.

Polyaniline membranes can also be used for the separation of carboxylic acid-water mixtures, through a process called pervaporation. Whereas undoped polyaniline displays relatively poor selectivities, fully HCl-doped polyaniline selectively permeates water over acetic acid. Separation factors, α, of >1300 for 50 wt% acetic acid/50 wt% water through doped polyaniline put it among the most selective membranes reported for acetic acid-water separations. Water transport through doped polyaniline is favored because of a combination of favorable diffusion, which is due to water's small size, and favorable solubility, which is due to the hydrophilicity of polyaniline induced by doping. Doped polyaniline effectively blocks larger carboxylic acids, such as propionic, but the smaller carboxylic acid,

formic, permeates to some extent. Pervaporation of a mixture of these three carboxylic acids and water confirms that doped polyaniline is effective at blocking acetic and propionic acids. Proton NMR has been demonstrated to be a sensitive quantitative technique for the analysis of these aqueous acid feeds and permeates. The relatively low permeation rates obtained with dense polyaniline membranes can be readily improved by forming asymmetric films or by increasing the feed temperature.

The separation of enantiomers of amino acids and drugs is important, especially since the physiological effects of different enantiomers may differ significantly. We have discovered that doping polyaniline with a chiral acid, followed by its removal with base, creates a novel chiral form of polyaniline. This new material has the ability to discriminate between a racemic mixture of d- and l-phenylalanine, an amino acid used as a precursor to several pharmaceuticals. This ability of chiral polyaniline as an enantioselective material is now being explored in detail. Patent protection has been sought through UC Los Angeles.

Refereed Publications

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Guo, H., C.M. Knobler, and R.B. Kaner, "A Chiral Recognition Polymer Based on Polyaniline" (to be published in *Synth. Met.*).

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Mattes, B.R., H.L. Wang, and D. Yang, "Electrically Conductive Polyaniline Fibers Prepared by Dry-Wet Spinning Techniques," *Soc. Plastics Eng. Proc., ANTEC 97* I, 1463 (1997).

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Ball, I.J., S.-C. Huang, and R.B. Kaner, "Permeabilities and Diffusion Coefficients of Common Solvents in Polyaniline Membranes," *Polym. Mater. Sci. Eng.* 77, 359 (1997).

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Ball, I.J., S.-C. Huang, and R.B. Kaner, "Polyaniline Membranes for Liquid Separations," Society for Plastic Engineering, Atlanta, GA, April 29, 1998 (invited).

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9821

Chlamydia Trachomatis Sequence Diversity in the Immunologic Major Outer Membrane Protein: Analysis of Mutation Trends and Evolutionary and Sequence-Structure/Function Relationships

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Abstract

Chlamydia trachomatis is an obligate intracellular bacterium that is the leading cause of sexually transmitted diseases in the developed world. The major outer membrane protein (MOMP) of *C. trachomatis* is the most antigenically diverse and abundant surface protein of the organism. It is a transmembrane protein that has become a major focus of research because it contains neutralizing determinants; elicits T-cell help for antibody production; contains serovar-, subspecies-, and species-specific epitopes; and may play a role in the attachment and invasion of host cells and in determining cell tropism. Until recently, MOMP was considered a conserved protein with only 15 variants (serovars) as defined by immunotyping. Now it is known that the gene that encodes MOMP (*omp1*) varies considerably among serovars and that many isolates of a given serovar can be identified by their unique "nucleotide signature." The presence of such variation presents a considerable challenge to vaccine development because MOMP is the primary candidate for a chlamydial vaccine. Further, structural determinations defined by crystallography and electron microscopy are not available for chlamydiae.

We propose to sequence 500 samples that represent genital samples from patients in five different cities in the United States and analyze the *omp1* and MOMP sequences by identifying mutation trends and covariation and by determining evolutionary and sequence-structure/function relationships. We will also compare the sequences with transmembrane proteins from other organisms. Evolutionary analyses that encompass phylogenetics will contribute to an understanding of the divergence of *omp1*; this may provide some insight into potential emergence of more or less pathogenic strains and the association of unique characteristics of specific genotypes with clinical and biologic data. Identifying covariance will be important because coordinate mutations at specific sites may impart a change in biologic properties that may provide a map for identifying functional determinants. In addition, sequences with highly covariant amino acids may define structural/functional sites that confer a selective advantage for the organism; statistical representation of sequence-structure correlations will help to determine structural/functional connections between positions. Representative peptides or DNA could then be selected for inclusion in a "cocktail" vaccine that would be broadly cross-reactive. *C. trachomatis* has not previously been analyzed in this way. Thus, this research will contribute to the molecular and biologic understanding of this important pathogen and will form the basis for a grant from DOE or the National Institutes of Health.

The goals of FY 1998 have been met. Over 500 *omp1* sequences of *C. trachomatis* genital strains have been sequenced and aligned in Mase, forming the database for the analyses described in this proposal. Using Rind, we generated phylogenetic trees where clustering of C with H and J *omp1* genotypes

suggested emergence of unique genotypes. These genotypes have been identified as variants of prototype genotypes and are being analyzed using cladistic and phenetic analyses with statistical measures to verify the significance of the findings. Using signature pattern analyses, we have identified unique genotypes within a genotype group for covariance and structure/function analyses. Covariance analysis will predict structure/function relationships for identifying immuno-logically important peptides for a mixed peptide or DNA vaccine that would be broadly cross-reactive.

9823

Transcription Element Organization in Drosophila

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Abstract

The length of a protein binding site in general spans a half-turn on the DNA double helix (i.e., roughly 5 to 6 base pairs) and provides a low sequence specificity ranging from 1 in 600 to 1 in 2100. In order to increase the sequence specificity, multiple binding sites can be presented to serve as one regulatory element. One such example is the drosophila HB1 element that consists of three homeodomain binding sites in tandem. Different homeodomain proteins bind to HB1 and result in different responses corresponding to the transcriptional element (e.g., Ubx activates and abd-A represses the corresponding gene product). Using a homology modeling approach, we have modeled the structures of both Ubx and abd-A homeodomain proteins, as well as the complexes of these protein binds to DNA. The structures of HB1 complexes, with three homeodomain proteins each, bind to their putative structures and are used in the study of the sequence-specificity of different homeodomain proteins, as well as the effects in the binding of multiple proteins to the spatial arrangements of the binding sites.

9824

Development of Thin-Film Phosphors for Flat-Panel Displays by Chemical Vapor Deposition

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Abstract

The worldwide market for flat-panel displays (FPDs) is projected to grow from \$7.3 billion this year to over \$35 billion in the year 2000 and would represent half of all high-information content display sales. One of the largest obstacles to the development of FPDs is the lack of phosphors (inorganic luminescent materials) with desired performance characteristics. High luminous intensity (brightness), color saturation, high energy efficiency, and short decay times are some of the properties that must be optimized for these new applications. Many of the commercial phosphors available are sulfide based and are unsuitable for the FPDs currently under development. Oxide phosphors represent the most promising solution to the replacement of sulfide-based materials, as they have excellent thermal stability, are radiation hard, can be produced in a variety of morphologies (powders, fibers, and films), and pose no outgassing problems. Thin-film phosphor layers fabricated through an unexplored, low-cost technique such as metallorganic chemical vapor deposition (MOCVD) would represent a breakthrough for the burgeoning FPD industry as an alternative phosphor screen to the more usual powder screens.

We constructed a MOCVD reaction chamber and identified the optimal conditions to fabricate europium-doped yttrium oxide luminescent thin films. Metallorganic vapor deposition of crystalline, fluorescent europium-doped Y_2O_3 was achieved with yttrium or europium tris (2,2,6,6-tetramethyl-3,5-heptanedionate) precursors deposited on sapphire, alumina, and glass substrates held between 400°C and 700°C. Growth rates of up to 0.5 mm/hour were achieved. The as-deposited films had high purity and contained only yttrium, europium, and oxygen peaks, as identified in the XPS spectra. The as-deposited films were red-emitting (611 nm) in the as-synthesized state. When excited with an electron gun, luminescence could be detected at voltages as low as 800 V, indicating that the quality of the as-deposited films was high. The films were also luminescent under ultraviolet radiation. Under both excitation sources, the films showed the characteristic fluorescence spectrum of the europium 3+ ion. The photoluminescent emission intensity of the films increased with increasing deposition temperature and with isothermal post-annealing time. Both were correlated with an increase in crystallite size. Although photoluminescent emission intensity has been found previously to be related to high-temperature treatments, this work shows that the major effect on luminescence intensity is the increase in crystallite size and not other thermal mechanisms.

Refereed Publications

Bacalski, C.F., M.A. Cherry, G.A. Hirata, J. McKittrick, and J. Mourant, "The Effect of Fuel to Oxidizer Ratio on the Luminescent Properties

and Particle Morphology of Combustion Synthesized Europium Activated Barium Magnesium Aluminate" (to be published in *J. Soc. Inf. Disp.*).

McKittrick, J., L.E. Shea, I.S.R. Sastry, and C. Bacalski, "Synthesis of Phosphors via Rapid Exothermic Reactions," in *Luminescent Materials VI*, C.R. Ronda and T. Welker, Eds. (The Electrochemical Society, Pennington, NJ, 1998) pp. 22–36.

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Bacalski, C.F., M.A. Cherry, G.A. Hirata, J. McKittrick, and J. Mourant, "The Effect of Fuel to Oxidizer Ratio on the Luminescent Properties and Particle Morphology of Combustion Synthesized Europium Activated Barium Magnesium Aluminate," Third International Conference on the Science and Technology of Display Phosphors, Huntington Beach, CA, November 3–5, 1997 (contributed).

Hirata, G.A., J. McKittrick, R. Sze, J. Mourant, K. Hubbard, S. Pattillo, K. Salazar, M. Trkula, and T.R. Gosnell, "Surface Crystallization of Luminescent Materials via Pulsed Laser Processing," Third International Conference on the Science and Technology of Display Phosphors, Huntington Beach, CA, November 3–5, 1997 (contributed).

McKittrick, J. "Materials Issues for the Next Generation of Emissive Flat Panel Displays," Integrated Microelectronics and Packaging Symposium, San Diego, CA, November 2, 1998 (invited).

McKittrick, J., "Synthesis of Low Voltage Phosphors for Field Emission Devices," Phosphor Technology Center of Excellence, Georgia Institute of Technology, Atlanta, GA, February 9, 1998 (invited).

McKittrick, J., "Synthesis, Processing and Characterization of Phosphors for Flat Panel Display Applications," Society for Information Display, San Diego, CA, May 27, 1998 (invited).

McKittrick, J., G.A. Hirata, M. Trkula, S.G. Pattillo, K. Hubbard, K. Salazar, and T.S. Moss, "Synthesis and Characterization of Rare-Earth Activated Thin Film Phosphors," 100th Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 4, 1998 (contributed).

9825
Magnetic Microstructures

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Abstract

The fabrication of new materials, in unusual configurations, drives many studies in condensed-matter physics and is behind many novel technologies. This proposal relates to comprehensive studies of novel magnetic microstructures, from investigation of growth through quantitative structural studies, exploration of novel physical properties produced by new geometries, and magnetic characterization at the atomic level. We are preparing interesting magnetic systems in configurations such as single, bilayers, and superlattices, and we are investigating many of their important magnetic properties. These studies are combined with quantitative neutron-scattering studies to characterize the magnetic structure at the atomic level.

The importance and rationale of the studies proposed here are that the understanding of many (if not all) interesting magnetic phenomena in microstructures relies on a detailed knowledge of the magnetic structure. From the technical standpoint, the studies performed under this grant have a direct impact on the materials involved in magnetic sensing and recording technologies. It is therefore important to understand the role magnetic and physical structures play in the improvement of these devices and the changes that occur when these devices are miniaturized. Generally, the implicit assumption is that the bulk magnetic structure is preserved, even in these unusual geometries that approach atomic length scales. This assumption is clearly incorrect. There are very few probes that can give detailed information regarding the magnetic structure at interfaces and surfaces. Neutron scattering is probably the most powerful of them, although synchrotron radiation has also been used with some success to address these problems. This project brings together two groups with complementary expertise; researchers at UC San Diego are preparing and measuring physical and structural properties, and Los Alamos scientists are characterizing the microscopic magnetic structure.

We have prepared and characterized structurally and magnetically and performed neutron scattering of many ferromagnetic (Fe)-antiferromagnetic (FeF_2 or $MnFe_2$) bilayers, which exhibit an important phenomenon denoted as exchange bias. Understanding exchange bias requires a detailed, quantitative knowledge of the magnetic structure of the interface. This structure is generally assumed to be the same as that in the bulk. To develop a thorough understanding, we have varied the crystallographic orientation, interfacial roughness, and growth conditions of the samples. Qualitative interpretation of the data suggests that the reversal of magnetization in these samples is accompanied by the formation of magnetic domains in the ferromagnet, contrary to widely held belief that magnetization reversal arose from the domains in the antiferromagnet. Further understanding requires the development of quantitative models and refinement techniques, which is underway at present. Our neutron-scattering work was carried

out at the National Institute of Standards and Technology and the Los Alamos Neutron Science Center (LANSCE) facilities after beam-time-allocation committees wrote extremely favorable reviews of our proposed work plans. In fact, the entire user program involving the polarized neutron reflectometer 1998–1999 run-cycle at LANSCE focused on solving the exchange bias problem investigated under the present CULAR program.

9826

Identification of Prostate Adenocarcinoma Tumor Suppressor Genes on Chromosome Arm 16q24.3

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Abstract

The effort proposed in this project is designed to study DNA isolated from human prostate tumor tissue, so as to identify a tumor suppressor gene that is hypothesized to exist in a 2-megabase region in the human genome at chromosome 16q24.3.
To attain this objective, we shall identify all genes in this region of the genome and test prostate gland mRNA for expression of each gene in normal tissue and in neoplastic tissue. The first step in the process of gene identification is to identify the smallest common region that could contain the genes by performing allelotyping on DNA extracted from prostate adenocarcinoma tissues from a number of cases after prostatectomies. This entails identifying markers (STSs) within the 16q24.3 region and performing polymerase chain reaction (PCR) amplification on DNA extracted from each tumor, as well as from benign tissue of the same donor. Comparison of the amount of each allelic marker by

acrylamide gel electrophoresis allows the allelic ratio for tumor tissue compared with that of the benign tissue. Tumors which have lost one copy of the DNA in the marker regions are identified by this means, generally called loss of heterozygosity (LOH). By mapping the LOH in a large number of prostate cancer cases, the smallest region of common deletion is defined.

During the past year, we devised a new method for identifying regional loss of DNA copies. This method, called quantitative microsatellite analysis (QuMA), uses real-time fluorescence analysis of PCR to quantify the number of copies at each STS as in LOH but does not require electrophoresis. Thus, QuMA is more rapid and less expensive to perform than LOH and provides the same kind of information. This method was developed and applied to a number of test samples to confirm its reliability. It now is being applied to a number of prostate tumors to define a region of common deletion that is smaller than the known region of 2 megabases.

Genes in the smaller region are being defined by searching the human genome data bases and by comparative sequencing of mouse and human genome in the syntenous region (which is chromosome 8 in the mouse). We will test candidate genes for expression in prostate tumor tissues by quantitative reverse transcriptase-PCR, using real-time fluorescence PCR in a manner similar to that described above for DNA copy number. Any gene that is expressed in normal prostate tissue and is not expressed in the tumor tissues will become a prime candidate as a tumor suppressor gene that is commonly inactivated in prostate cancer.

If such a gene is identified, it will be characterized as to sequence and by function. Such knowledge about a tumor suppressor gene could be used by researchers to define the etiology of the disease and could be used in the clinics to help in diagnosis and prognosis of individual patients. In addition, clinical researchers may also use this information for effective gene therapy of prostate cancer. Such progress would be beneficial to the Laboratory and DOE in justifying their efforts in human genome ordering and sequencing. It confirms the need for sequence information in performing translational research on functional genomics. This benefits the UC San Francisco Cancer Center by contributing to better prognostication and therapy for prostate cancer, which is the most common nonskin malignancy in males in the United States and the second most common mortality cancer in males in the United States.

Refereed Publication

Ginzinger, D.G., T.E. Godfrey, J. Nigro, D. Moore, M.G. Pallavicini, and R.H. Jensen, "Measurement of DNA Copy Number at Microsatellite Loci Using Quantitative Real Time PCR Analysis" (submitted to *Proc. Natl. Acad. Sci.*).

Presentations

Ginzinger, D.G., T. Godfrey, and R.H. Jensen, "Quantitative Allele Analysis (QuAAn); A Novel Method to Enumerate DNA Copy Number of Many Allele throughout the Genome Using TaqMan," Meeting of the Applied Biosystems Sequence Detection Systems Users, Foster City, CA, May 18–19, 1998 (invited).

Ginzinger, D.G., T. Godfrey, J. Nigro, M. Pallavicini, and R.H. Jensen, "Measurement of DNA Copy Number at Microsatellite Loci in Humans and Inbred Mice Using Quantitative Allele Analysis (QuAAn)," Meeting of the American Society of Human Genetics, Denver, CO, October 27–31 (contributed).

Ginzinger, D.G., T. Godfrey, J. Nigro, M. Pallavicini, and R.H. Jensen, "Regional DNA

Copy Number Enumeration in Tumors Using Real Time PCR Analysis," Seminar, UC San Francisco Cancer Center, September 4, 1998 (invited).

Ginzinger, D.G., T. Godfrey, J. Nigro, D. Moore, M. Pallavicini, and R.H. Jensen, "Measurement of DNA Copy Number at Microsatellite Loci Using Quantitative Real Time PCR Analysis," Seminar, University of Washington Department of Medical Genetics, Seattle, WA, December 10, 1998 (invited).

9827

Investigation of Metal-Oxide Magnetic Artificial Structures

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Abstract

The discoveries of the oscillatory magnetic coupling and the giant magnetoresistance (GMR) in magnetic nanostructures stimulated a great deal of activity within the physics community because of their high potential for applications in the magnetic-recording industry. Compared with the ~1% magnetoresistance in conventional magnetic-recording materials, the much higher value of the GMR (10% to 100%) in the new class of materials obviously creates a great

potential in making highly sensitive magnetic sensors. In fact, GMR heads are becoming the dominant products in the market. Recently, colossal magnetoresistance was also discovered in oxide materials. It is now well recognized that development of magnetic nanostructure research will have a significant impact on the science and technology.

As an artificial structure is reduced to the nanometer scale, the quantum size effect will manifest itself. It is believed that the essential physics behind the oscillatory magnetic coupling and the GMR is the formation of the quantum well (QW) states in the magnetic nanostructures. To a certain extent, the development of the magnetic nanostructures depends on the understanding of the QW states in these structures. The objective of this project is to explore the fundamental properties of the QW states and their connection to the newly discovered GMR technology.

Last year, we initiated the QW research at the Advanced Light Source at Lawrence Berkeley National Laboratory. Photoemission serves as the best technique to study the QW states in momentum space. The high brightness and the small beam size at the Advanced Light Source provides a unique capability for combining wedged samples with photoemission. This combination allows us to explore the fundamental behavior of the QW states at the atomic level.

Figure 1 shows the photoemission results on a double-wedge sample. This structure allows the independent control of the copper QW thickness and the nickel-probe-layer position inside the copper QW. The intensity oscillations along the AC diagonal direction show the QW states at the Fermi level. The oscillations along the BD diagonal direction show the amplitude variation of the quantized electron waves inside the copper QW as probed by the nickel layer.

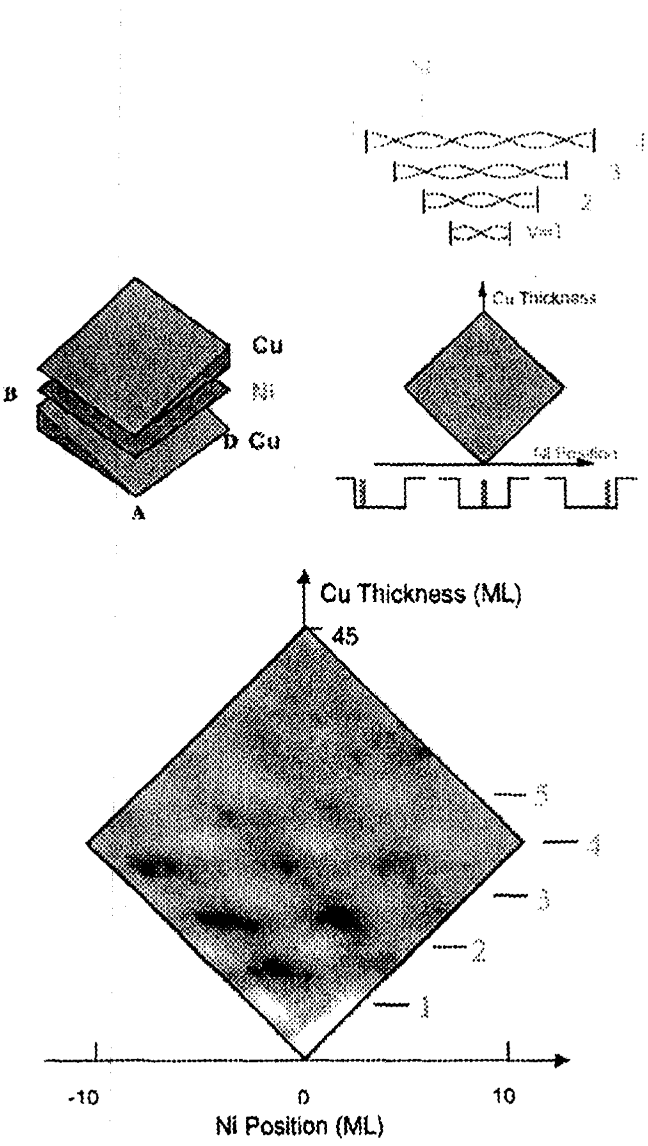

Fig. 1. Photoemission results on a double-wedge sample.

Figure 2 is another example of the photoemission measurement on a wedged sample. Panels 2(a) and 2(b) show the QW states at the Fermi level from different positions of the copper Fermi surface in Cu(100) grown on a 15-ML layer of Co(100). Panel 2(c) is the magnetic measurement after another 3-ML cobalt film was grown on top of the copper to form a Co/Cu/Co sandwich. The oscillatory magnetic coupling between the two ferromagnetic cobalt layers across the copper

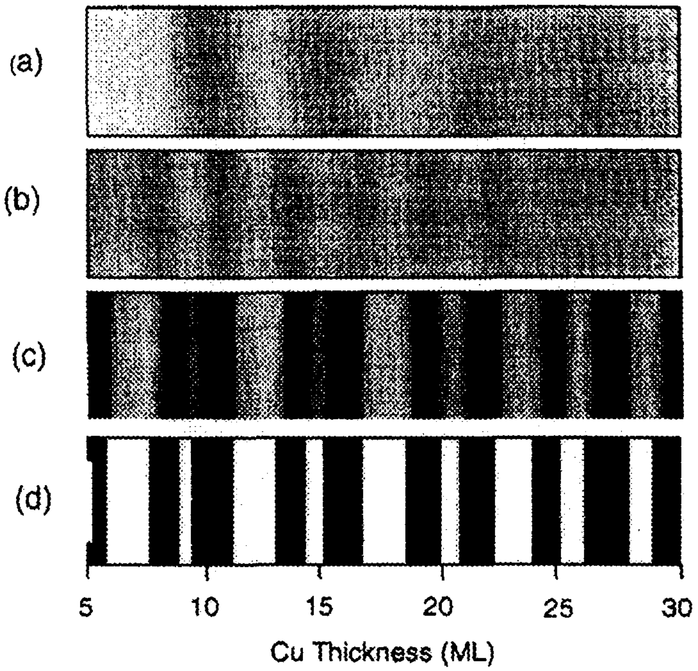

Fig. 2. Photoemission measurement on a wedged sample.

manifests as the alternation of the magnetization direction of the top 3-ML cobalt film. This was measured by magnetic x-ray linear dichroism and shown as the bright and dark stripes in panel 2(c). We than calculated the interlayer coupling from the QW information from panels 2(a) and 2(b). The calculated result in panel 2(d) agrees very well with the experiment. This result demonstrates that the interlayer magnetic coupling is determined by the QW states in the momentum space.

As stated in the proposal, our ultimate goal is to combine the efforts of our group and the Los Alamos group to develop the magnetic nanostructures. We are currently building up a compact sample-preparation chamber that will accelerate the developmental progress in the next year. Then, various types of nanostructures, such as the magnetic tunneling junctions, can be readily fabricated and investigated.

Refereed Publications

Kawakami, R.K., E. Rotenberg, Ernesto J. Escorcia-Aparicio, Hyuk J. Choi, J.H. Wolfe, N.V. Smith, and Z.Q. Qiu, "Determination of the Magnetic Coupling in the Co/Cu/Co(100) System with the Momentum Resolved Quantum Well States" (submitted to *Phys. Rev. Lett.*).

Kawakami, R.K., E. Rotenberg, Hyuk J. Choi, Ernesto J. Escorcia-Aparicio, M.O. Bowen, J.H. Wolfe, E. Arenholz, Z. Zhang, N.V. Smith, and Z.Q. Qiu, "Quantum Well States in Cu Thin Films Probed by an Atomic Layer of Ni," *Nature* **398**, 132 (1999).

Zhang, Z.D., Hyuk. J. Choi, R.K. Kawakami, Ernesto Escorcia-Aparicio, Martin Bowen, Jason Wolfe, E. Rotenberg, N.V. Smith, and Z.Q. Qiu, "Oscillatory Coupling between Co Films across Cu/$Ni_{30}Cu_{70}$/Cu(100) Double Quantum Wells" (submitted to *Phys. Rev. Lett.*).

9828

Development and Characterization of Novel Conjugated Polymer/ Semiconductor Nanoparticle Composite Materials

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Abstract

During the period of October 1997 to September 1998, we made good progress on several fronts of the project. The main development was in the synthesis and identification of nanoparticles and polymers that have the desired properties for developing the composite materials of interest. Specifically, we have been searching for strongly luminescent nanoparticles that are potentially useful for light-emitting-diode applications. Among the different nanoparticle systems examined, including CdS, CdSe, ZnS, Cu_xS, PbI_2, PbS, TiO_2, and Fe_2O_3, the most promising appears to be CdS, CdSe, and ZnS. We are currently developing synthetic strategies to embed these nanoparticles in conjugated and nonconjugated polymers, since it turns out that to make such composite films with good optical and morphological qualities is not trivial. We have been testing different synthetic methods, including ion exchange in a polymer matrix, to make high-quality composite films.

For nanoparticles that are not luminescent or are weakly luminescent, we have been exploring their applications for photovoltaic devices, primarily in solar cells. Among the different nanoparticles examined, TiO_2 appears to be most promising for this application. For TiO_2-based solar cells, one of the major problems encountered is that the liquid electrolytes currently used are difficult to seal and often limit charge transport. To help solve this problem, we had tested several prototypical TiO_2-based solar cells using polymeric electrolytes. We had also explored different dye molecules that are promising as sensitizers for TiO_2 solar cells.

For the polymeric materials, we had focused on poly[2-methoxy, >5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene], or MEH-PPV, and polyfluorenes because they are relatively well characterized and are familiar to researchers involved in this project. In addition, the samples are readily available from our existing collaborators. For the composite material containing both nanoparticles and conjugated polymers, it is likely that the signal observed in the femtosecond studies will have contributions from both materials, which may complicate the interpretation of the data. Therefore, we need to first study the nanoparticles in transparent nonconjugated polymers in which there is no signal from the polymer. We had successfully embedded CdS and ZnS nanoparticles in various nonconjugated polymers including ploy(methyl methacrylate) and poly(vinyl alcohol). The films look promising, but they clearly need improvements in terms of optical quality.

We are currently examining different preparation methods to obtain better-quality films.

To study the charge carrier dynamics using broadband femtosecond pump-probe spectroscopy of several samples we have identified to date, one of the graduate-student researchers involved in this research visited Los Alamos for a week in July 1998 to conduct experiments. Some very interesting results have been obtained, and a manuscript to report the results is currently in preparation.

In addition, we have applied femtosecond transient absorption to directly measure the population/depopulation dynamics of the lowest (1S) and the first excited (1P) electron states in CdSe nanocrystals of different radii with 1S-1P energy separation up to 16 longitudinal optical phonon energies. Instead of the drastic reduction of the energy relaxation rate expected as a result of a phonon bottleneck, we observe a fast subpicosecond 1P-to-1S relaxation, with the rate enhanced in nanocrystals of smaller radii. This indicates the opening of new confinement-enhanced relaxation channels that likely involve Auger-type electron-hole energy transfer. This work has been published.

Refereed Publications

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Klimov, V., and D.W. McBranch, "Femtosecond 1P-to-1S Electron Relaxation in Strongly Confined Semiconductor Nanocrystals," *Phys. Rev. Lett.* **80**, 4028 (1998).

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Klimov, V.I., C.J. Schwartz, D.W. McBranch, and C.W. White, "Initial Carrier Relaxation Dynamics in Ion-Implanted Si Nanocrystals: Femtosecond Transient Absorption Study," *Appl. Phys. Lett.* 73, 2603 (1998).

Klimov, V.I., C.J. Schwarz, D.W. McBranch, C. Leatherdale, and M. Bawendi, "Ultrafast Dynamics of Inter- and Intra-band Transitions in Semiconductor Nanocrystals" (submitted to *Phys. Rev. Lett.*).

McBranch, D.W., B. Kraabel, S. Xu, R.S. Kohlman, V.I. Klimov, D.D.C. Bradley, B.R. Hsieh, and M. Ruhner, "Signatures of Excitons and Polaron Pairs in the Femtosecond Excited-State Absorption Spectra of Conjugated Polymers and Oligomers" (to be published in *Synth. Met.*).

Patel, A.A., and J.Z. Zhang, "Synthesis and Ultrafast Characterization of PbS Semiconductor Nanoparticles: Control and Effects of Size, Shape, and Surface" (submitted to *J. Nanotechnol.*).

Sengupta, A., B. Jiang, K.C. Mandal, and J.Z. Zhang, "Ultrafast Electronic Relaxation Dynamics in PbI_2 Semiconductor Colloidal Nano-Particles: A Femtosecond Transient Absorption Study" (submitted to *J. Phys. Chem.*).

Nonrefereed Publication

Roberti, T.W., "Femtosecond Studies of Charge Carrier Dynamics in II–VI Semiconductor Nano-Particles: CdS, CdSe, and ZnS," Ph.D. thesis, University of California at Santa Cruz (1998).

Presentations

Zhang, J.Z., "Femtosecond Studies of Charge Carrier Dynamics in Metal and Semiconductor Colloidal Nano-Particles," 33rd Western Regional Meeting, Pacific

Conference on Chemistry
and Spectroscopy, Irvine, CA,
October 21–25, 1997 (invited).

Zhang, J.Z., "Femtosecond Studies of Charge Carrier Dynamics in Semiconductor and Metal Nanoparticles," University of Pittsburgh, Pittsburgh, PA, February 1998 (invited).

Zhang, J.Z., "Femtosecond Studies of Electron Dynamics in Semiconductor and Metal Colloidal Nano-Particles: AgI and Au," Symposium on Frontiers of Chemistry, The Hong Kong University of Science and Technology, Hong Kong, December 20–23, 1997 (invited).

Zhang, J.Z., "Femtosecond Studies of Electronic Relaxation Dynamics in Metal Nano-Particles: Effects of Size and Surface," Meeting of the American Physical Society, Los Angeles, CA, March 16–20, 1998 (invited).

Zhang, J.Z., "Femtosecond Studies of Excited State Dynamics of Polyenes and Conjugated Polymers," Carnegie Mellon University, Pittsburgh, PA, February 1998 (invited).

Zhang, J.Z., "Femtosecond Studies of Exciton Dynamics in Magnetic Semiconductor γ-Fe_2O_3 Colloidal Nano-Particles," Symposium on Frontiers of Chemistry, The Hong Kong University of Science and Technology, Hong Kong, December 20–23, 1997 (contributed).

Zhang, J.Z., "Femtosecond Studies of Exciton Dynamics in Quantum-Confined Systems: Nano-Particles and Conjugated Polymers," Gordon Research Conference on Electronic Processes in Organic Materials, Newport, RI, July 26–31, 1998 (contributed).

Zhang, J.Z., "Ultrafast Studies of Charge Carrier Dynamics in Nano-Materials," Beijing University, Beijing, China, December 1997 (invited).

Zhang, J.Z., "Ultrafast Studies of Charge Carrier Dynamics in Semiconductor and Metal Colloidal Nanoparticles," San Jose State University, San Jose, CA, November 1998 (invited).

Zhang, J.Z., and L. Howe, "Femtosecond Studies of Excited State Dynamics of Photosensitizers at the Liquid-Micelle Interface," Meeting of the Electrochemical Society, San Diego, CA, May 3–8, 1998 (invited).

McBranch, D.W., "Ultrafast Probes of Quantum-Confined Materials: Semiconductor Nanocrystals and Semiconducting Polymers," University of California at Santa Cruz, Santa Cruz, CA, January 20, 1999 (invited).

McBranch, D.W., "Universal Features in the Transient Absorption of Phenylene-Based Polymers," International Conference on Science and Technology of Synthetic Metals, Montpellier, France, July 1998 (invited).

9829
Transport in Non-Fermi Liquids

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Abstract

The nature of the proposed research is basic research in the area of materials science. The research is directed toward the understanding of electronic properties of novel materials such as cuprate superconductors and other strongly correlated materials. The transport properties of these materials require a new approach, which is fundamentally different from that of the Fermi liquid theory that has been the backbone of the theory of conventional metals. Recently, transport in correlated disordered systems has taken a new turn. From experiments in semiconducting devices, it has been convincingly demonstrated that there can be a metal-insulator transition in two dimensions. This transition at zero temperature is a quantum critical point that reflects a fundamental change of the quantum mechanical ground state of the correlated two-dimensional electron gas. For decades, such a transition was thought to be impossible. We have made considerable progress in understanding this problem.

Transport in the novel high-temperature superconductors remains an intriguing problem that offers a clue to the mechanism of superconductivity in these novel materials. We examined the theory that the change of the electronic kinetic energy in a direction perpendicular to the CuO-planes (c-axis) in high-temperature superconductors is a substantial fraction of the condensation energy. It was argued that the consequences of this theory based on a rigorous conductivity sum rule are consistent with recent optical and penetration depth measurements. In addition, it was shown that this theory accounts for two striking features of c-axis optical measurements: (1) the observation that the c-axis kinetic energy is substantially reduced in the superconducting state and (2) the correlation between penetration depth and conductivity in the normal state.

Considerable progress was made in understanding the effect of impurities in high-temperature superconductors. The impurities are known to suppress superconducting transition temperatures, and, therefore, the understanding of impurity effects is very important. Similarly, progress in the understanding of the effect of impurities has led to novel ideas regarding the symmetry properties of the energy gap parameter, for example a state that violates parity and time-reversal symmetries.

Refereed Publications

Chakravarty, S., H.-Y. Kee, and E. Abrahams, "Frustrated Kinetic Energy, the Optical Sum Rule, and the Mechanism of Superconductivity" (submitted to *Phys. Rev. Lett.*).

Chakravarty, S., L. Yin, and E. Abrahams, "Interactions and Scaling in a Disordered Two-Dimensional Metal," *Phys. Rev. B: Rapid Comm.* 58, R559 (1998).

Chakravarty, S., S. Kivelson, C. Nayak, and K. Voelker, "Wigner Glass, Spin Liquids and the Metal-Insulator Transition" (to be published in *Philos. Mag.*).

Presentations

Balatsky, A.V., "Electronic Properties and P and T Violation in Cuprates," Strongly Correlated Electron Systems Winter School, Taiwan, January 1998 (invited).

Balatsky, A.V., "Marginal Stability of d-Wave Superconductors," Stripes 1998, Rome, Italy, June 1998 (invited).

Balatsky, A.V., "Marginal Stability of d-Wave Superconductors," Strongly Correlated Electron Systems, Paris, France, July 1998 (invited).

Balatsky, A.V., "Marginal Stability of d-Wave Superconductors," Workshop on Strongly Correlated Electrons," Hamamatsu, Japan, December 1998 (invited).

Balatsky, A.V., "Spontaneous Violation of Parity and Time Reversal in d-Wave Superconductor," Workshop on High-Temperature Superconductivity, Aspen, CO, Summer 1998 (invited).

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Balatsy, A.V., "Spontaneous Violation of Parity and Time Reversal in d-Wave Superconductor with Magnetic Impurities," Materials and Mechanisms in Superconductivity, Baton Rouge, LA, February 1998 (invited).

Chakravarty, S., "c-Axis Conductivity Sum Rule in High Temperature Superconductors," Many Body Workshop, Los Alamos National Laboratory, Los Alamos, NM, August 1998 (invited).

Chakravarty, S., "The Conductivity Sum Rule in High Temperature Superconductors," Aspen Center for Physics, Aspen, CO, July 1998 (invited).

Chakravarty, S., "The Metal-Insulator Transition through the Wigner Glass," Conference on Disorder and Interactions in Quantum Hall and Mesoscopic Systems, ITP, Santa Barbara, August 1998 (invited).

Chakravarty, S., "The Metal-Insulator Transition through the Wigner Glass," Gordon Research Conference on Correlated Systems, New Hampshire, July 1998 (invited).

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Growth of Thermal Barrier Coatings: Complementary Modeling and Deposition Studies

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Abstract

This program aims to advance the understanding of the evolution of critical microstructural features in thermal barrier coatings (TBCs) produced by E-beam physical vapor deposition (EB-PVD). TBC performance relies on the architecture of the microstructural porosity, with long ribbonlike intercolumnar voids dictating the strain tolerance and finer intracolumnar pores influencing the thermal conductivity. Currently, none of the existing models for growth of PVD films can predict the relevant microstructural features or account for the influence of the crystallographic texture on the evolution of the porosity. The program involves growth experiments and computer simulations, with the ultimate goal of developing predictive relationships between the process parameters and the microstructure/properties.

Substantial progress has been made in both our understanding of the physical characteristics of the problem, as well as in identifying the relevant issues and challenges posed by the modeling activity. Experiments to date have focused on deposition on stationary substrates at temperatures of 900°C to 1100°C and rates of 1 to 4 μm/min, to establish a materials response base line against which the effects of geometry and substrate manipulation can be assessed. Initial modeling activities have focused on the atomistic processes using atomic ballistic deposition (ABD). Salient findings are briefly described below.

- The primary mechanism responsible for the formation of porosity is the shadowing produced by the interaction of the vapor flux with the topography of the growth surface. This process occurs at two distinct length scales. Intercolumnar voids arise from the vapor interaction with the column tips, typically on the scale of a few micrometers, whereas intracolumnar pores are a consequence of the interplay with much finer-scale features on the growth surface, e.g., the ledges propagating along the active crystallographic facets.

- Porosity can evolve even in the absence of substrate rotation, as long as there is a finite component of oblique incidence in the vapor flux. Porosity was detected even under nominally normal incidence at $T \sim 0.46\ T_M$, at which the established microstructure zone maps predict a fully dense columnar morphology. This suggests that deviations of only a few degrees

from normal incidence are sufficient to induce porosity that cannot be completely healed even when surface diffusion is very active.

- Modeling activities incorporating surface diffusion in an ABD model revealed that oblique vapor incidence angles lead to the formation of porosity even at temperatures where normal incidence results in dense structures, in agreement with the experimental observations.
- For deposition under normal incidence, there is a distinct change in the crystallographic orientation of the columns, from ⟨111⟩ to ⟨110⟩, when the temperature is increased from 900°C to 1100°C. However, oblique deposition promotes the ⟨110⟩ texture at all temperatures within the above range. The cumulative evidence suggests that there is a fundamental change in the growth mechanism within this temperature range. The ⟨111⟩ growth takes place with the active facets normal to the column axis in a pattern reminiscent of island growth, whereas the ⟨110⟩ growth involves the same active facets but oriented at an oblique angle from the column axis, forming a distinct "rooftop" tip morphology.
- The pattern of intercolumnar porosity in samples deposited under oblique incidence is substantially refined as the deposition temperature decreases from 1100°C to 900°C, reflecting a change in the scale and morphology of the column tips occurring concomitantly with the change in texture.
- The above findings suggest that the key role of substrate manipulation is not in producing shadowing, but rather in tailoring the pattern of shadowing around the column tips and perhaps in influencing the selection of a specific texture. Modeling activities using ABD have also shown how substrate rotation can influence the pattern of intra-columnar porosity, in agreement with experimental observations in the literature.

Ongoing experimental activities in the program address the specific effects of substrate rotation and deposition rate, in the context of the base line established by the stationary substrate results. The modeling work is evolving toward the linkage of the atomistic processes with the mesoscopic (column) growth scale. This will build on emerging Hyper-MD models being developed at Los Alamos to bridge the relevant time scales.

Refereed Publication

Terry, S.G., J.R. Litty, and C.G. Levi, "Evolution of Porosity and Texture in Thermal Barrier Coatings Grown by EB-PVD," in *Elevated Temperature Coatings: Science and Technology III*, J.M. Hampikian and N.B. Dahotre, Eds. (TMS, Warrendale, PA, in press).

Presentations

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Terry, S.G., J.R. Litty, and C.G. Levi, "Microstructural Evolution in Thermal Barrier Coatings Grown by Physical Vapor Deposition,"

Symposium on Recent Advances in Processing and Characterization of Thermal Barrier Coatings, Meeting of the Pacific Coast and Basic Sciences Division of the American Ceramic Society, Irvine, CA, October 21–24, 1998 (invited).

Terry, S.G., J.R. Litty, D. Stave, and C.G. Levi, "Microstructural Evolution of EB-PVD TBCs. II: Crystallographic Texture," TBC Winter Workshop '99, University of California Santa Barbara, Santa Barbara, CA, January 6–8, 1999 (contributed).

Terry, S.G., J.R. Litty, M. Pusch, D.R. Clarke, and C.G. Levi, "Microstructural Evolution of EB-PVD TBCs. I: Porosity," TBC Winter Workshop '99, University of California Santa Barbara, Santa Barbara, CA, January 6–8, 1999 (contributed).

9831

The Role of Copper in Bacterial Manganese(II) Oxidation

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Abstract

It is well recognized that the production of nuclear weapons and release of toxic byproducts to the environment, whether intentional or inadvertent, has led to significant organic, metal, and radionuclide contamination of soils, sediments, and groundwater at various DOE sites in the United States. Developing strategies for remediating metal and radionuclide pollution represents a difficult challenge and one that has not been widely addressed. Microorganisms interact with metals and radionuclides in a variety of ways and thereby affect their biogeochemical cycling. The fact that some of these interactions lead to a reduction in the mobility, bioavailability, and toxicity of the metals and radionuclides suggests that natural

biogeochemical processes might be exploited for metal and radionuclide bioremediation. However, in most cases the biochemical mechanisms by which bacteria transform metals are poorly understood.

Microbial Mn(II) oxidation is a naturally occurring biogeochemical process that could be used as an in situ pathway for enhancing the immobilization of metals and radionuclides or for the degradation of a variety of organic contaminants. However, little is known about the biochemical mechanisms involved in manganese oxidation. Previous research on three unrelated Mn(II)-oxidizing bacteria has suggested (on the basis of gene sequencing) that proteins related to the multicopper oxidase family of proteins catalyze Mn(II) oxidation. The proposed research seeks to elucidate the role of copper in Mn(II) oxidation and to determine whether copper has a universal role in bacterial Mn(II) oxidation. Because most known copper oxidases are involved in the oxidation of organic compounds, Mn(II)-oxidizing multicopper oxidases may represent a new type of copper oxidase.

Our goals this year were to obtain sufficient amounts of one Mn(II)-oxidizing protein in a form that is pure enough for spectroscopic analysis and to initiate comparative studies of Mn(II)-oxidizing proteins from other bacteria. The primary aim of the spectroscopic analysis was to determine the number and types of copper atoms in the Mn(II)-oxidizing protein and their structural parameters. The aim of the comparative studies was to screen different Mn(II)-oxidizing bacteria to test the universal role of copper in Mn(II) oxidation and to identify other proteins with suitable properties (especially ease of purification and recovery of activity) for detailed investigation. We developed a protocol for purifying a protein from one Mn(II)-oxidizing bacterium in active form and designed a procedure for purifying sufficient quantities for the spectroscopic studies. The plan is to obtain sufficient protein for detailed analysis at Los Alamos in FY 1999. We also screened a number of other Mn(II)-oxidizing bacteria for genes coding proteins similar to the multicopper oxidases that we have already identified, and we found several strains that seem to possess homologues. Future studies may explore the purification and characterization of these proteins.

The research is highly multidisciplinary, building upon the strengths of both UC San Diego and Los Alamos. The expertise and facilities at both institutions are highly complementary for the proposed work and the research represents new but related directions for research programs at both locations. A Los Alamos–UC San Diego collaborative proposal related to this research was submitted to the DOE NABIR program. Although this was unsuccessful, we intend to resubmit it for the next request for proposals. We believe that this research presents exciting opportunities and is of practical value to the DOE.

Nonrefereed Publication

Tebo, B.M., and L.M. He, "Microbially Mediated Oxidative Precipitation Reactions," in *Mineral-Water Interfacial Reactions: Kinetics and Mechanisms*, T. Grundl and D.L. Sparks, Eds. (American Chemical Society, Washington, DC, in press).

Presentation

Francis, C.A., and B.M. Tebo, "Identification of a Manganese-Oxidizing Protein from Spores of a Marine Bacillus," Meeting of the American Society for Microbiology, Atlanta, GA, May 17–21, 1998 (contributed).

9832

Neutron Diffraction Measurements of Bulk Internal Strains in TiAl-Based Low-Symmetry Structural Composite Materials

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Abstract

While neutron diffraction is the only technique that can make spatially resolved, phase specific, nondestructive strain measurements in the interior of bulk components, our ability to use neutron scattering to examine the structure and properties of materials is limited by our ability to analyze and interpret the information contained in neutron diffraction patterns. Whereas Los Alamos researchers have contributed to advancements in analysis of pulsed neutron scattering data, significant challenges exist in extracting quantitative information on the structure and mechanical properties of grossly anisotropic materials. This is especially true when studying materials that have complex or graded microstructures or multiphase materials that are heterogeneous, such as advanced engineering composites. At the computational end, recent advances in computational methodologies can now predict the microstructure sensitive development of intrinsic strains and stresses inside thick anisotropic TiAl-based composites. However, such predictions are largely uncorroborated because of the lack of experimental means to probe at subsurface levels (i.e., deeper than 100 μm). Such composite material interrogations can be radically improved by integrating novel neutron diffraction–based experimental methods with recent developments in computational modeling of microstructural effects in complex materials.

Research Objectives and Goals

The objective is to combine the unique neutron scattering capabilities at the Los Alamos Neutron Science Center (LANSCE) with the existing strength at UC San Diego in the areas of advanced materials theory and computational micromechanics, to create a novel experimental-theoretical-computational tool for directly measuring and interpreting the development of internal stresses in two-phase γ-TiAl+α_2-Ti$_3$Al low-symmetry composite materials (LSCM). The low-symmetry results in severe internal constraints and stresses that affect both constitutive response and material toughness (i.e., ductility and fracture resistance). Thus, the specific research objectives are exploring the evolution of internal stresses during (a) thermomechanical processing-induced phase transformations, (b) deformation and subsequent in-service loading, and (c) thermal cyclic excursions, in two-phase γ-TiAl+α_2-Ti$_3$Al LSCM, with the ultimate goal of correlating them with predicted and observed mechanical response in service.

Micromechanical modeling of TiAl-based composite materials at UC San Diego has provided a quantitative framework for analyzing deformation and fracture in these materials,[1,2] which are being further developed through a combined experimental study of processing and service-induced internal stresses and their corresponding mechanical response and fracture at service conditions. A technologically important goal of this collaboration between UC San Diego and Los Alamos is to directly correlate experimentally measured internal stress states with those predicted by our crystal models, for a variety of deformation and thermal histories, to provide a deeper quantitative and predictive capability. This capability will allow us, for the first time, to directly probe the internal stress states in these materials and, in turn, to provide a unique tool for studying composite materials.

Scientific and Technical Impact

An expected outcome of the project is the development of a fundamentally unique, quantitative approach to probing and interpreting internal strains and stress states, for the specific purpose of formulating models of deformation and fracture and validating them, directly studying complex phenomena, and attaining a detailed understanding of the role of internal, as-processed constraints in anisotropic composite materials on deformation and fracture response.

Neutron diffraction may emerge as the most reliable validation method for predictive material models. The use of neutron diffraction to explore the vital effects of internal stresses, toward the development and eventual use of technologically important TiAl-based composite materials, is expected to highlight the unique contributions of such a national resource. This is in accordance with the Department of Energy's vision of establishing LANSCE as an indispensable research and development tool.

References

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Refereed Publication

Kad, Bimal, Robert Asaro, Bjorn Clausen, and Mark Bourke, "Neutron Diffraction Measurements of Internal Strains in TiAl-Based Alloys" (submitted to *Proc. Int. Symp. Gamma Titanium Aluminides*).

Presentations

Kad, Bimal, Robert Asaro, Bjorn Clausen, Mark Bourke, "Neutron Diffraction Measurements of Internal Strains in TiAl-Based Alloys," Annual Meeting of The Minerals, Metals, and Materials Society, San Diego, CA, February 28–March 4, 1999 (contributed).

Kad, Bimal, Mark Daymond, Hahn Choo, and Mark Bourke, "Neutron Diffraction Measurements of Internal Strains in TiAl-Based Alloys," Meeting of the Materials Research Society, Boston, MA, November 30–December 4, 1998, (contributed).

9833

Charge and Magnetic Ordering in Transition Metal Complex Oxides

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Abstract

We are investigating the physics of complex electronic materials based on transition metal oxides, which are tunable, by controlling doping, temperature, pressure, etc. The fact that these materials show functionality for electronic, optical, and magnetic properties is the key to an exciting future of science and applications. The understanding of the basic physics and the influences of interactions and dimensionality on those functionalities are still lacking, but they can be accomplished by a close collaboration between UC Riverside and the theory group at Los Alamos and by direct interactions with experimentalists at Los Alamos and elsewhere.

The modern era of materials synthesis control and advances in measurement and modeling techniques have made it clear that "multiscale" complexity is intrinsic to complex electronic materials. This complexity needs to be controlled and exploited (rather than avoided) for increasingly stringent demands of technology. The spatial and temporal complexity is driven by strong (often competing) couplings of spin, charge, and lattice controlled by electron-electron interactions, dimensionality, disorder, etc. The phenomena of charge localization and ordering in the tunable classes of materials that we propose to study is a prime example of this complexity in transition metal oxides with functionality for electronic, optical, and magnetic properties.

We have studied three main problems:

- The competition between long-range Coulombic and short-range antiferromagnetic dipolar interactions and its impact on charge ordering in layered transition metal oxides. It was shown by extensive numerical simulations that the phase diagram of layered antiferromagnetic compounds is very complex and includes striped, mesoscale charge-ordered phases that have been observed experimentally.
- Destruction of superfluid density in layered cuprates by non-magnetic impurities. We have shown that nonmagnetic impurities destroy superfluidity in high-temperature superconductors due to pinning of fluctuating stripes.
- The interplay between magnetism and Kondo physics in *f*-electron systems. It was shown that the interplay between magnetic interactions and magnetic screening (Kondo effect) gives rise to a new phase of matter (Griffiths phase) which was recently observed experimentally.

Refereed Publications

Castro Neto, A.H., and A.V. Balatsky, "Effect of Planar Impurities on the Superfluid Density of Striped Cuprates" (submitted to *Phys. Rev. Lett.*).

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Stojkovic, Branko P., Z.G. Yu, A.R. Bishop, A.H. Castro Neto, and Niels Gronbech-Jensen, "Charge Ordering and Long-Range Interactions in Layered Transition Metal Oxides" (submitted to *Phys. Rev. Lett.*).

Presentations

Castilla, G., A.H. Castro Neto, and B.A. Jones, "Non-Fermi Liquid Behavior and Griffiths Phase in Rare Earth Compounds," Meeting of the American Physical Society, Los Angeles, CA, March 1998 (contributed).

Castro Neto, A.H., and F. Guinea, "Superconductivity, Josephson Coupling, and Order Parameter Symmetry in Striped Cuprates," International Conference on New Theories, Discoveries, and Applications of Superconductors and Related Materials, Louisiana, February 1998 (invited).

Castro Neto, A.H., and F. Guinea, "Superconductivity, Josephson Coupling, and Order Parameter Symmetry in Striped Cuprates," Meeting of the American Physical Society, Los Angeles, CA, March 1998 (contributed).

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Castro Neto, A.H., G. Castilla, and B.A. Jones, "Griffiths Singularities and Non-Fermi Liquid Behavior in *f*-Electron Compounds," International Conference on Strongly Correlated Electron Systems, Paris, France, July 15–18, 1998 (invited).

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9834

Synthesis and Characterization of Novel Biologically Grown Nanocrystallites

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Abstract

The work of the team at Los Alamos National Laboratory has concentrated on comparative studies of nonlinear-optical response and ultrafast carrier dynamics in nanocrystals (NCs) prepared at UC Riverside by the bio-route and colloidal NCs synthesized at Massachusetts Institute of Technology by the organometallic route. Both types of NCs exhibit similar NC-size dependent features in linear absorption spectra. However, despite this similarity, the nonlinear-optical properties and carrier relaxation in bio-generated and chemically generated NCs are significantly different because of the difference in surface passivations. Relaxation dynamics in bio-NCs are much faster than in colloidal NCs, indicating a lower degree of passivation of electron surface traps. The enhanced surface trapping in bio-NCs leads to a modification

in optical nonlinearities that are dominated by excited-state absorption involving surface defects. This is in contrast to optical nonlinearities in colloidal NCs, which are almost solely due to state-filling-induced bleaching of optical transitions between NC quantized states.

The work at UC Riverside has concentrated on the fabrication and preliminary characterization of biologic-ally capped NCs, or bio-NCs. We have prepared ZnS, CdS, CdSe, and Pbs bio-NCs, using a variety of biological capping materials including cysteine, glutathione, phytochelatins, and DNA. Interestingly, variation in the sizes of DNA did not significantly alter the nature and sizes of the bio-NCs formed. Cysteine, glutathione, and phytochelatins were potent capping materials for ZnS and CdS. It was possible to change surface passivation in particles formed with glutathione. Both cysteine and phytochelatins were able to displace glutathione from the surface of the particles. Photodegradation experiments with a model compound suggest that bio-NCs were significantly more effective than TiO_2 in degradation of *p*-nitrophenol.

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Klimov, V.I., C.J. Schwartz, D.W. McBranch, C. Leatherdale, and M. Bawendi, "Ultrafast Dynamics of Inter- and Intra-Band Transitions in Semiconductor Nanocrystals: Implications for Quantum-Dot Lasers" (submitted to *Phys. Rev. Lett.*).

Klimov, V.I., C.J. Schwartz, X. Yang, D.W. McBranch, C. Leatherdale, and M. Bawendi, "Electron and Hole Relaxation Pathways in II–VI Semiconductor Nanocrystals" (to be published in *Mater. Res. Soc. Symp. Proc.*).

Nguyen, L., R. Kho., W. Bae, and R.K. Mehra, "Glutathione as a Matrix for the Synthesis of CdS Nanocrystallites," *Chemosphere* **38**, 155 (1998).

Torres-Martinez, C., R. Kho, L. Nguyen, W. Bae, V. Klimov, and R.K. Mehra, "Biomolecularly Capped, Uniformly Sized Nanocrystalline Materials: GSH-Capped ZnS Nanocrystals" (submitted to *Nanotechnology*).

Presentations

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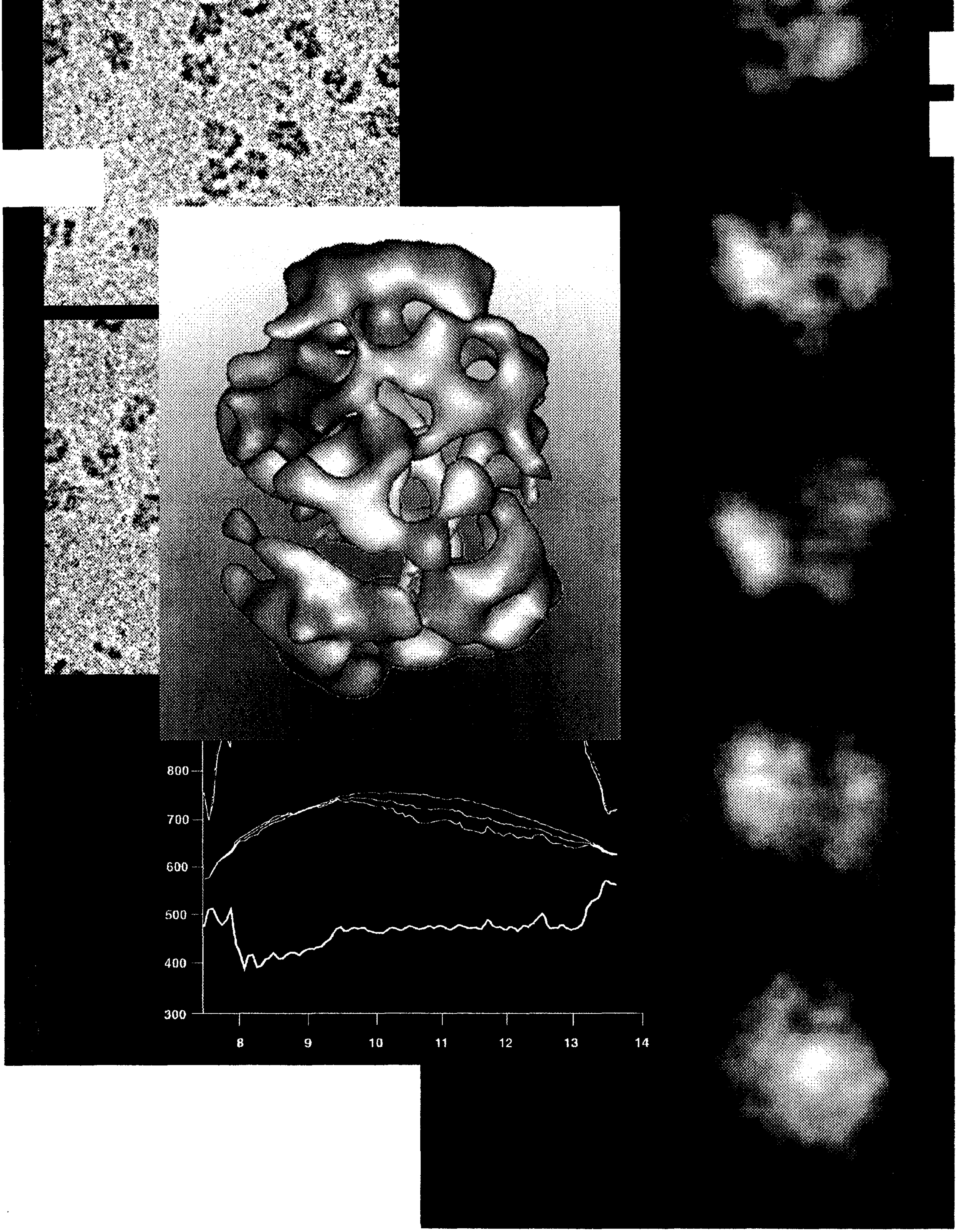
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University of California Research Partnership Initiative (UCRPI) Progress Reports

UCRPIs use UCDRD funds to foster the development of joint research activities and capabilities that are of strategic interest to Los Alamos National Laboratory and that have the potential for external funding. The goal is to strengthen activities so that they can become self-sustaining through external funding. No formal call for proposals is issued. Proposals are submitted to the UC Coordination Office at Los Alamos, which makes recommendations to the Laboratory Director. As funds become available, proposals are selected from those that have been received. Priority is given to those projects that strengthen the strategic directions and core competencies of the Laboratory and that result in establishing or strengthening important collaborations. Additional details of the program are available at on the World Wide Web at http://stb.lanl.gov/uc.

Of the thirty-two UCRPIs funded in FY 1998, nineteen were new projects and thirteen were continuing projects from the previous fiscal year. Twenty-six project reports, with listings of personnel, publications, patents, and awards for FY 1998 follow in this section.

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Final Reports

Special Research Programs

00 9851 Frontiers of Materials Science Program:
Neutron Scattering and Vibrational Probes of Structure in Layered and Perovskite CMR Materials
Dimitri Argyriou, Los Alamos;
Geoffrey F. Strouse, UC Santa Barbara

00 9853 Frontiers of Materials Science Program:
Molecular Density and Orientation in Confined Polymer Layers under Static and Dynamic (Flow) Conditions
Gregory Smith, Los Alamos;
Tonya Kuhl, UC Santa Barbara

00 9855 Frontiers of Materials Science Program: Investigations of the Structures of Microtubule-Based Cellular Motors Using Neutron Scattering
Rex Hjelm, Los Alamos;
Robert Mendelson, UC San Francisco

00 Research and Education Utilizing the National High Magnetic Field Laboratory (NHMFL): Overview
Gregory S. Boebinger, Los Alamos

00 9845 Research and Education Utilizing the NHMFL:
Physics of Quantum Hall Devices in Ultra-High Magnetic Fields
Yongmin Kim, Los Alamos;
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00 9864 Research and Education Utilizing the NHMFL:
Neutral Fermions at Filling Factor 1/2
Greg Boebinger, Los Alamos;
Dung-Hai Lee, UC Berkeley

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A LANL/UCLA Joint Experiment on the Generation of Coherent Infrared Radiation at the LANL Advanced Free-Electron Laser Facility

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Graduate Students: M. Hogan, A. Tremaine, S. Anderson, P. Frigola, and A. Murokh, UC Los Angeles

Abstract

We report observation of high free-electron-laser (FEL) gains, greater than 10^5 in a single pass, in recent self-amplified spontaneous emission experiments performed with the advanced FEL high-brightness, 17-MeV electron beam. Our experiments confirm theoretical predictions of FEL operating in the high-gain, single-pass regime. We also observed evidence of the electron microbunching on the length scale of the infrared wavelength.

Background

A free-electron-laser (FEL) approach called self-amplified spontaneous emission (SASE) has recently received considerable interest because of the possibility of applying this technique to the generation of high-intensity, coherent x-rays. The SASE process relies on a very long wiggler in which an electron beam amplifies its own spontaneous emission and the radiation grows exponentially with distance in the wiggler. With a sufficiently long wiggler, high gains can result from the strong interaction between the electron beam and the light it emits. The gain, or amplification factor, first grows linearly and then exponentially with the wiggler length until it reaches saturation (Fig. 1). Although large SASE gain has been demonstrated in the millimeter-wave region, experiments at shorter wavelengths have up to now produced single-pass gains of less than 10. The collaboration between Los Alamos and UC Los Angeles (UCLA) was aimed at demonstrating large SASE gain in the infrared with the use of the high-current, high-brightness electron beam from the advanced FEL (AFEL) in conjunction with very long wigglers, one built at Los Alamos and the other provided by UCLA.

Progress

In these high-gain SASE experiments, the high-current, low-emittance electron beam from the AFEL photoinjector was focused to a small spot at the entrance of the wigglers. The first wiggler had a 1-m-long uniform section and was built at Los Alamos. The second wiggler was 2 m long and was built at UCLA. Both wigglers produced radiation in the 12- to 16-μm region, the infrared part of the spectrum. We showed that the infrared radiation power measured at a distance from the wiggler evolved from low-power spontaneous emission to high-power SASE as we varied the beam current. By fitting the measured infrared energy versus current to an analytic model, we obtained the single-pass gain versus current (Fig. 2). At a beam current of 260 A, the Los Alamos wiggler with a 1-m uniform section has a single-pass gain of 300. With the UCLA wiggler, we measured a gain greater than 10^5, the largest single-pass gain ever observed in the infrared region.

In a follow-up experiment, we introduced a thin aluminum foil in the electron beam path at the end of the wiggler. The SASE process caused the electron beam to clump together with a period of the infrared wavelength. We observed evidence of this microbunching process from the coherent transition radiation emitted by the bunched electron beam. The observation of this radiation with all the characteristics of the coherent generation of light validates our earlier measurement of high gain and confirms the existence of microbunching as predicted by the SASE theory.

The success of this project already has had a significant impact on the international effort toward short-wavelength FELs. The observation of large single-pass gains demonstrates unequivocally the SASE principle and is an important milestone in the collaborative effort to extend SASE toward the x-ray region. This effort, called the Linac Coherent Light Source, is a collaboration involving the Stanford Linear Accelerator Center, UCLA, Brookhaven National Laboratory, Los Alamos, Argonne National Laboratory, and Lawrence Livermore National Laboratory to demonstrate the generation of a beam of picosecond coherent x-rays. These coherent x-ray beams will benefit many areas of basic research such as high-field atomic and molecular physics, the exploration of high-energy-density phenomena, and the study of ultrafast dynamics of important biological molecules.

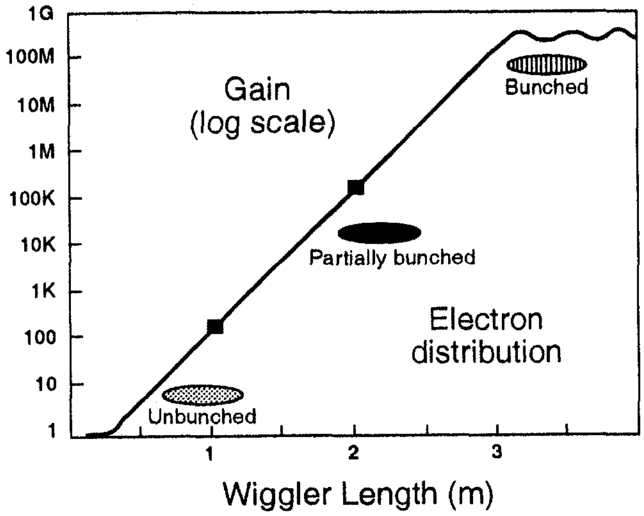

Fig. 1. Illustration of the SASE gain (on logarithmic scale) versus wiggler length. The electron density distributions for the three cases—unbunched (low gain), partially bunched (exponential gain), and bunched (saturation)—are depicted in the three ellipses. Our experimental data were taken at the 1-m and 2-m wiggler lengths (marked by solid squares).

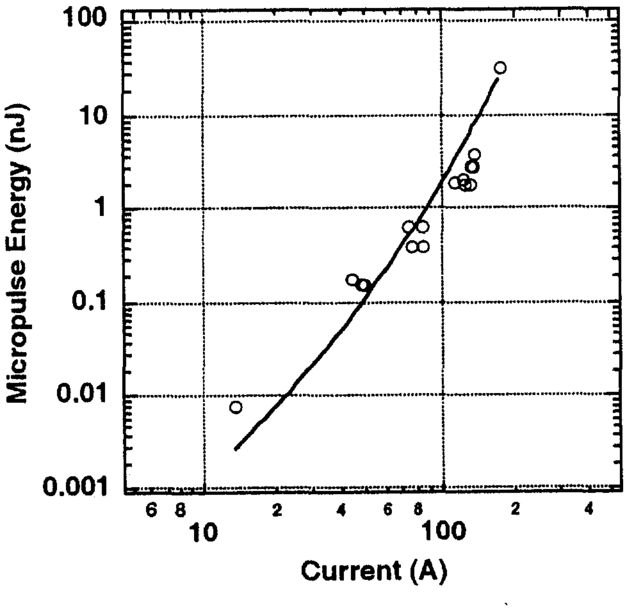

Fig. 2. Log-log plot of SASE pulse energy versus current for the 2-m wiggler. The gain at the highest current is 2×10^5, the highest FEL gain in the infrared.

Refereed Publications

Hogan, M., C. Pellegrini, J.B. Rosenzweig, S. Anderson, P. Frigola, A. Tremaine, C. Fortgang, D.C. Nguyen, R.L. Sheffield, J. Kinross-Wright, A. Varfolomeev, A.A. Varfolomeev, S. Tomachev, and R. Carr, "Measurement of Gain Larger than 10^5 at 12 μm in a Self-Amplified Spontaneous Emission Free-Electron Laser," *Phys. Rev. Lett.* **81**, 4867 (1998).

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Tremaine, A., J.B. Rosenzweig, S. Anderson, P. Frigola, M. Hogan, A. Murokh, D.C. Nguyen, and R.L. Sheffield, "Observation of Self-Amplified Spontaneous Emission-Induced Electron Beam Microbunching Using Coherent Transition Radiation," *Phys. Rev. Lett.* **81**, 5816 (1998).

Conferences

Hogan, M., "The UCLA/LANL High-Gain SASE Experiment," 18th International Free-Electron Laser Conference, Williamsburg, VA, August 17–21, 1998 (invited).

Hogan, M., "The UCLA/LANL Ultra-High-Gain SASE Experiments," Meeting of the American Physical Society, Columbus, OH, April 18–21, 1998 (invited).

Nguyen, D.C., "High-Gain SASE Experiments in the Infrared," 18th International Free-Electron Laser Conference, Williamsburg, VA, August 17–21, 1998 (invited).

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Tremaine, A., "FEL Microbunching Measured Using Coherent Transition Radiation," 18th International Free-Electron Laser Conference, Williamsburg, VA, August 17–21, 1998 (contributed).

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Silicon Metabolism in Diatoms

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Abstract

This project involves an ongoing collaboration, taking advantage of unique facilities and capabilities at Los Alamos and UC Santa Barbara, in which new materials and methods are developed and applied to the laboratory and field study of marine diatom species and their influence on global climate and geochemical cycles. Diatoms are the main primary producers in most coastal marine systems. It is estimated that they contribute to more than 40% of the total marine primary productivity. These photosynthesizing organisms therefore represent a major sink for atmospheric carbon dioxide. Besides the usual nutrients (carbon, nitrogen, phosphorus, etc.) required by autotrophic phytoplankton, diatoms also have an obligate requirement for silicon during critical parts of their cell cycle. Several models reveal that silicon could be the limiting nutrient for diatom proliferation in certain marine environments, thereby significantly influencing the level of primary productivity in those systems. In some instances, when silicon becomes the limiting nutrient in an algal bloom, other much less benign species, especially toxin-producing dinoflagellates, can become dominant. A quantitative understanding of the physiology of silicon use by diatoms and the role of silicon nutrient limitation on marine algal blooms is thus of practical environmental importance.

To date, there have been several significant products of the collaboration, which was begun under a LACOR grant. We have developed methods for production of silicon-32 in high specific activity for use as a radiotracer in diatom nutrient studies. Four patents have been issued and one refereed publication has resulted from this work. We have developed and tested new radioanalytical techniques for quantitative measurement of absolute and kinetic uptake of silicic acid by diatoms in the laboratory and in the field. This work is described in two refereed publications. We also presented pertinent aspects of the work at a National American Chemical Society Meeting. We have extended the collaboration to international recognition, with both principal investigators serving on the organizing committee of an international workshop on the application of various tracers to marine biogeochemical cycles that will be held in late 1999 or early 2000. We have obtained support for continuation of the collaboration through the Department of Energy Office of Biological and Environmental Research (OBER), and we continue to develop proposals to extend radioanalytical techniques to the precise correlation of silicon uptake data to carbon primary production. In the last year of the collaboration, we have used funding from OBER to hire a postdoctoral fellow to accomplish this work. These methods will provide new data pertinent to models developed for understanding the role of diatoms in determining global climate. This collaboration supports research goals of both the Department of Energy and the

National Science Foundation in the area of climate and environmental research. The work will have significance both from a basic science perspective and for establishment of national policy relative to the effect of greenhouse gases on global climate.

Background

In the initial phase of the collaboration, UC Santa Barbara queried Los Alamos about the availability of silicon-32 in high specific activity. Research at UC Santa Barbara focused on measuring biogenic silicon production by marine diatoms and relating this to primary productivity by these organisms in the oceans. The application of the radiotracer to this work was being investigated as a substitute for stable mass-spectroscopic isotopic tracer methods. The spectroscopic methods required substantial amounts of laboratory work-up and time, so that the volume of data that could be generated from an oceanographic research cruise was significantly limited. The plan was to develop new radioanalytical methods that would enhance both the quality and quantity of data. At the time of the inquiry, Los Alamos research had recently developed methods for production and recovery of aluminum-26 from potassium chloride targets that had been irradiated at the Los Alamos Linear Proton Accelerator. Though the isotope had not been specifically recovered, it was suspected that scientifically significant amounts of silicon-32 were co-produced with the aluminum-26 in these targets. Since the silicon-32 is a pure beta-emitting nuclide, it was necessary to develop an effective chemical recovery process to evaluate the production yield and isotopic quality. Using support from separate sources, including the DOE Office of Isotope Production and Distribution and the National Science Foundation, the principal investigators worked together to develop a process that yields a high-quality silicon-32 isotopic product with excellent properties for biological oceanographic studies.

In order to take full advantage of the radiotracer, it was necessary to develop radioanalytical techniques that could be combined with the oceanographic methods. Under a LACOR grant, the researchers from Los Alamos and UC Santa Barbara again combined expertise and unique facilities to develop a new radioanalytical method that allows rapid quantitative analysis of dynamic silicon nutrient up-take by diatoms. The new method was successfully tested in an oceanographic cruise in Monterey Bay, California, in 1995. Silicon nutrient uptake data was correlated with other carbon and nitrogen nutrient data collected during the cruise. Results of the work described above are summarized in the closeout report for the LACOR-funded collaboration.

Though valuable, the nutrient correlations are limited in both accuracy and precision because the incubations for each different nutrient study were performed on separate oceanographic water samples (multi-bottle incubations). We have proposed that radioanalytical methods can be developed and refined in such a way that single-bottle incubations can be done using multiple radiotracers to remove intersample variability and thereby enhance the quality of nutrient correlations to primary productivity.
In order to support expansion of the collaboration into this next phase, we were granted Los Alamos UCDRD funding in FY 1997 to develop a detailed proposal to seek external funding to support the technical development of the concept of single-bottle radioanalytical tracer studies. A proposal titled "Impact of Silicon Metabolism in Diatoms on Mediating Carbon and Nitrogen Cycles" was jointly developed. In May of 1997, the proposal was submitted to the Department of Energy in response to DOE Notice 97-09: Biotechnological Investigations—Ocean Margins Program. Though the proposal received favorable reviews, it did not receive funding under this notice, primarily because the reviewers believed it did not precisely meet the specific objectives of the call. However, management personnel in the DOE

Office of Energy Research (OBER Biophysical Research) believed that the development of new radioanalytical methods for this application met some general objectives in the technical portfolio of that office and encouraged us to develop a brief proposal to gain support for a post-doctoral fellow to continue this aspect of the collaboration. A brief proposal titled "New Multi-Tracer Methods in Biological Oceanographic Research" was submitted. In response to this proposal, the DOE OBER Biophysical Research Program allocated $90,000 to the Laboratory to fund a postdoctoral fellow under this collaboration.

Progress in 1998

At present, the postdoctoral position is a joint position at Los Alamos and the Monterey Bay Aquatic Research Institute (MBARI). In this dual appointment we are able to take technologies into the field that are developed in the laboratory for the study of diatom metabolism. Our initial focus in the work being done at Los Alamos is to set up an incubation laboratory where we can develop and test dual label (carbon-14, silicon-32/phosphorus-32) radioanalytical techniques. These techniques will be used in the laboratory to help researchers understand the metabolism of bicarbonate, phosphate, and silicate as a function of the diatom cell cycle. Data collected in the laboratory can be applied in the field toward understanding the link between the silicon and carbon nutrient cycles in a quantitative way using single-bottle incubations. This capability has not previously existed.

We are also analyzing data collected in the Coastal Ocean Processes cruise of Monterey Bay made in the spring of 1995 to discover correlations between bicarbonate uptake (measured using carbon-14), nitrate uptake, and silicon uptake during a major upwelling event that caused extraordinary diatom blooms during the cruise. The analysis is not yet complete, but it will provide a framework in which to analyze the merits of single-bottle incubations versus multi-bottle incubations in order to understand relationships among the nutrients during field research on diatom nutrient uptake.

We assembled a Web site announcing a workshop on the production and application of tracers in oceanographic research. Originally, this workshop was to be held in August of 1999 at the Institut Universitaire Européen de la Mer in Brest, France. However, circumstances dictated that we postpone and relocate the workshop. We are now considering holding the workshop in early 2000 at one of the following locations: UC Santa Barbara, MBARI–Santa Cruz, or Los Alamos. Though the time and location will be different, the content will still be as described at the Web site address http://mwanal.lanl.gov:80/tracer99/. To date, we have had over 100 expressions of interest in the workshop.

Refereed Publications

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Brzezinski, Mark A., Dennis R. Phillips, Francisco P. Chavez, Gernot E. Friedrich, and Richard C. Dugdale, "Silica Production in the Monterey, California, Upwelling System," *Limnol. Oceanogr.* 42 (8), 1694 (1997).

Presentation

Phillips, D.R., M.A. Brzezinski, V.T. Hamilton, and R.M. Kudela, "Silicon-32: Diatoms, the Silicon Cycle, and the Climate," 216th National American Chemical Society Meeting, Symposium on AMS and the Oceans: Tracing Natural Processes with Rare Isotopes, Boston, MA, August 26, 1998 (contributed).

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Automating AIDS Research

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Abstract

Certain scientific problems pose major challenges, mainly because they require enormous amounts of information to make meaningful progress. In the area of infectious disease, the human immunodeficiency virus (HIV) poses such challenges. A simple estimate leads to the conclusion that there are at least millions, perhaps even billions, of genetically unique HIV viruses that are afflicting 32 million people throughout the world. Within the next few years, the enormous "swarm" of genetically unique viruses will likely infect more than 1% of the world's population—resulting in the leading cause of death (i.e., AIDS) due to an infectious agent. The ability to combat the HIV/AIDS problem will depend, in large part, on the ability to conduct an enormous number of laboratory-based tests that help with the development of drugs and vaccines.

One significant problem is that HIV laboratories with the necessary capacities (i.e., the firepower of hundreds of laboratory technicians) do not exist at present. Over the past three years, the objective of our program has been to develop a realistic blueprint for building such twenty-first century laboratories. The strategy for building high-throughput laboratories is to use and integrate existing technologies from biology, engineering, computer science, and the Internet.

Our new design of a high-throughput automated laboratory is aptly described as "batch science via the Internet." The overall concept is to (1) use the Internet for communicating and interacting with the high-throughput laboratory from any geographic location in the world, (2) use shipping services (such as Federal Express) to deliver the large numbers of samples to the laboratory, (3) use existing robotic and automation technology to carry out the laboratory experiments in a batch mode, and (4) use database resources to deliver and organize enormous quantities of information to participating researchers. In the batch science scheme, all data are created in a digital format, which means that they can be made available to a larger number of researchers throughout the world.

In order to carry out batch science via the Internet, we envision software consisting of "process control tools" that are used to program and coordinate all the necessary activities. The process control tools are disclosed in the U.S. Patent No. 5,841,975, titled "Method and Apparatus for Globally-Accessible Automated Testing," which was granted during the undertaking of our project.

The batch science laboratory we envision for HIV research (with an experimental firepower equivalent to 100 laboratory technicians) could be running within two to three years. The facility would be capable of performing three major categories of laboratory tests in a highly flexible (programmable) manner: infectivity assays, cytotoxic cellular assays, and molecular-sequencing assays. With such tests, almost any major effort could be undertaken in drug and vaccine development.

Building a batch science laboratory fits into the range of intermediate-scale scientific undertakings (i.e., in the range of $10 million) that require some degree of consensus by the scientific community. This perspective has motivated us to organize a colloquium sponsored by the Institute of Medicine and the National Academy of Engineering. The colloquium, titled "Automation in Threat Reduction and Infectious Disease Research: Needs and New Directions," will be held at the National Academy of Sciences in Washington, D.C., on April 29–30, 1999. The topics of the colloquium will include established and emerging infectious disease threats; food supply and environmental threats; biowarfare and bioterrorism threats; and applications beyond infectious diseases, such as molecular and genetic medicine. The goals of the upcoming colloquium are to develop scientific constituencies and funding mechanisms for moving forward with important problems that could benefit from batch science approaches.

Background

A major obstacle that HIV/AIDS researchers need to overcome is achieving a critical mass of information that enables therapeutics and vaccine developers to stay ahead. Overcoming this obstacle demands enormous quantities of basic research and has remained elusive with current laboratory approaches. Now, for the first time, a critical number of powerful technologies are at hand that will allow scientists to attack HIV/AIDS and emerging infectious diseases. Biologists have developed a variety of laboratory-based assays that are tremendously powerful and readily adaptable to large-scale efforts. Engineers have developed innovative robotic and automation technologies that can skyrocket the number and variety of laboratory experiments. Computer scientists have developed the World Wide Web, Internet programming languages, and network protocols that are transforming environments for scientific collaboration. The one step remaining is to merge these cross-disciplinary technologies for effective action on HIV/AIDS and emerging infections. Developing robotic hardware and Internet software tools that embody this crucial step is the specific aim of our program.

Successful research activities in the twenty-first century will proceed along two fronts. The first involves traditional models of hands-on research taking place in all infectious disease laboratories today. This type of activity is labor intensive and best suited to small-scale operations. The second involves newer models of high-volume research that are based on next-generation tools from applied robotics and automation. This type of strategy will provide researchers with massive experimental powers that generate enormous quantities of data. New breeds of scientific navigational tools that orchestrate these activities via the Internet will also make it possible, as never before, for HIV/AIDS and infectious disease researchers to collaborate and share key information on a worldwide scale. We characterize this second approach as "batch science via the Internet," because it permits researchers from any geographic location to submit sets of biologic samples and automated instrument instructions as coordinated units. This approach is distinct from virtual science via the Internet, where experiments are controlled from afar in real time.

Our program has four objectives: (1) to design and build new breeds of automated instruments and scientific navigational tools for conducting and coordinating HIV/AIDS research via the Internet; (2) to apply these technologies to ongoing basic and clinical investigations on HIV/AIDS; (3) to make these tools available to HIV/AIDS investigators on the widest scale possible; and (4) to extend the use of these innovations to emerging infections and other biological, medical, and chemical investigations.

There are significant benefits to the proposed program. First, the capability to conduct laboratory tests on a massive scale will help level the playing field against HIV's rapid mutation rate—enabling researchers to use altogether new approaches to developing vaccines and therapies. Second, the automated instruments will decrease the average cost of each test or assay by taking advantage of economies of scale made possible by automation. Conservatively, a two- to tenfold cost reduction is expected.

The strategy is to build instruments that will serve the greatest needs of researchers. Basic science, clinical trials, and vaccine research on HIV/AIDS rely mainly on three categories of laboratory-based experiments: (1) viral infectivity assays, which measure such things as antibody blocking activities (humoral immunity), antiviral drugs potencies, and kinetic (physical-chemical) reactions of active HIV particles; (2) cytotoxic cellular assays, which measure cell-mediated killing (cellular immunity), cytokine activities, and processes dealing with antigen presentation; and (3) molecular-sequencing assays, which characterize the genetic makeup of cell-free and cell-associated viruses, either in selected regions or in full length. For each category of assay, one or two flexible automated instrument designs will increase the number of laboratory-based experiments that HIV/AIDS researchers demand for a global attack. At present, we plan to build several types of automated instruments for HIV/AIDS research. The first three instruments will perform quantitative HIV infectivity assays. The subsequent installment of instruments will perform quantitative cytotoxic cellular assays and amplify and sequence viral genes.

Our program entails close collaborations between Los Alamos National Laboratory and the University of California, Los Angeles (UCLA). These two institutions have complementary expertise essential to the success of this program.

Los Alamos is an international leader in the field of laboratory automation. Over the past decade, Laboratory researchers have designed and built a wide variety of automated laboratory instruments for programs such as the human genome, analytical chemistry, and radioactive materials handling. More important, they have also pioneered technologies for the next generation in automation, called the standard laboratory module (SLM), which constitutes the core technology for our proposed program.

UCLA has been at the forefront in HIV/AIDS and the development of the Internet. In 1981 the UCLA Medical Center was the first hospital to identify AIDS cases in the United States and since then, researchers associated with the UCLA AIDS Institute have continued pioneering work in the field. In 1969 UCLA became the first node on the ARPANET (now called the Internet), and since that milestone the computer science and engineering faculty have maintained forefront positions.

The structure for our program involves four complementary areas of activity:

- robotic hardware—building the SLM-based instruments and developing other types of high-throughput SLM-based instruments;
- Internet software—developing the scientific navigational tools for conducting and coordinating key processes at the researcher's home base as well as laboratory and database facilities;
- adapting basic science—quality control matters, standardization of assays, and the scaling-up of experiments so that automated instruments reach their greatest potential; and
- laboratory infrastructure—the design, operation, and maintenance of biohazard facilities dedicated to high-throughput infectious disease research.

In the area of robotic hardware, we have developed functional concepts for three highly-integrated instruments—dubbed the infectron, incutron, and detectron—that will work together. The design takes maximum advantage of existing commercial hardware, as well as specialized components that are adapted from other instruments at Los Alamos. The infectron will perform all the initial infectious operations for the quantitative HIV assays. The incutron will perform the incubation and feeding of assay cells. The detectron will perform all the detecting or scoring operations for the quantitative HIV infectivity assay.

The software for the automated instruments will operate on a three-tier hierarchy. At the lowest level, robotic modules possess SLM controllers that drive components like actuators, detectors, and servomotors and coordinate their internal electromechanical activities. At the intermediate level, task sequence controllers use tools from operations research to govern intricate flows of supplies and samples through automated instruments. At the highest level, process control tools that are created by our development program will help researchers carry out a spectrum of important activities via the Internet. To date, we have developed software that enables a number of proprietary instruments (including a Packard liquid-handling station, Beckman ORCA robot, and Los Alamos microtiter plate handler) to operate as SLM-compliant components. We have been awarded a patent for high-level software tools (called access, operation, documentation, submission, analysis, storage, and privileges) that coordinate a spectrum of user activities.

In the area of adapting basic science, we have identified highly flexible methods for performing quantitative HIV infectivity assays. The assays will use human cells that support the growth and detection of wild-type viruses, including peripheral blood mononuclear cells, monocytes/macrophages, and Langerhans cells. We have applied for patents on the automated testing of retroviral and biological specimens.

Concerning laboratory infrastructure, the proposed laboratory facility will include a receiving station that is adjacent to a low-temperature mass storage area for efficient handling of incoming samples. The biohazard space will include specialized housings for the automated instruments that contain aerosols and spills. The instrument housings will adjoin supply areas for loading assay materials and waste areas for handling contaminated materials. The facility will require sizable incubation and sterilization capabilities and will be designed with safety, efficiency, and dependability in mind.

Developing state-of-the-art automated instruments for HIV/AIDS research and emerging infectious diseases will not require a "Manhattan Project" as some might suspect. To the contrary, the program will involve a focused effort by a relatively small team of motivated engineers and scientists. First-generation instruments could be running within two years and second-generation clones (at a fraction of the initial cost) would follow soon thereafter. The first instruments will have the capability of performing the work of 100 laboratory technicians. Comparing the scale and efficiency of high-throughput automation to human-based labor reveals that development costs of up-and-running instruments would be recouped in less than five years. Cost breakdowns appear in our article published in *Nature Biotechnology*.

Progress

Our project has been marked by three significant milestones as follows.

Patents. In 1998 we were awarded a key U.S. Patent for "Method and Apparatus for Globally-Accessible Automated Testing." The patent contains 39 independent claims that describe the software-system architecture for batch science machines and also describes how to connect and program such machines over the Internet or secure intranets. Such descriptions are important because secure networks are commonly used by emergency-response teams, the military, and intelligence agencies. The patent is assigned to the University of California and serves to protect intellectual property of the University and its authors. In addition, the University is assisting us in applying for four other patents relating to batch science methodologies.

Major Publications. In 1998 we published several articles dealing with our research. An editorial that accompanied our article in *Nature Biotechnology* advocated that batch science could serve as the basis for more integrated solutions to dealing with multifaceted problems like bioterrorism. The journal called upon the biotechnology industry to consider other ways for reducing the threats of bioterrorism. Another article extends the concept of batch science to the broader notions of "batch manufacturing" and the convenient manipulating of matter over the Internet. Still another article describes how to create standard laboratory modules (SLMs) that announce their capabilities upon their hookup into larger automated instrument systems. Such announcements will result in SLMs that are truly plug-and-play.

Organization of a National Meeting. In August 1998, the presidents of the Institute of Medicine and the National Academy of Engineering and gave their approval for a jointly sponsored colloquium titled "Automation in Threat Reduction and Infectious Disease Research: Needs and New Directions." The colloquium is an outgrowth of our efforts over the last three years to accelerate the pace of research in areas pertaining to infectious diseases. We have assembled a 12-member organizing committee, which is composed of forward-looking scientists and engineers from around the country. We anticipate that 400 scientists and policymakers will attend the two-day colloquium at National Academy of Science headquarters in Washington, D.C., on April 29–30, 1999. The program will focus on the following topics: bioterrorism and biowarfare, established and emerging infections, threats to food supply and environment, and applications beyond infectious diseases. Goals for the upcoming colloquium are to develop scientific constituencies and funding mechanisms for moving forward with important problems that could benefit from batch science approaches.

Refereed Publications

Layne, S.P., and T.J. Beugelsdijk, "Laboratory Firepower for AIDS Research" (submitted to *Clin. Infect. Dis.*).

Layne, S.P., and T.J. Beugelsdijk, "Laboratory Firepower for Infectious Disease Research," *Nat. Biotechnol.* **16**, 825 (1998).

Layne, S.P., and T.J. Beugelsdijk, "Mass Customized Testing and Manufacturing via the Internet," *Rob. Comput. Integr. Manuf.* **14**, 377 (1998).

Staab, T.A., and G.W. Kramer, "The Device Capability Dataset: A Descriptive Approach to Laboratory Automation System Integration Standards," *J. Assoc. Lab. Autom.* **3**, 45 (1998).

Presentations

Elling, J., and T. Staab, "Annual Report from International Standardization Committees, ASTM," Lab Automation '98 Conference, San Diego, CA, January 17–21, 1998 (invited).

Schaefer, B., T. Staab, R. Schaefer, and J. Elling, "Standardized Control of Laboratory Equipment with the American Society of Testing and Materials (ASTM) Laboratory Equipment Control Interface Specification (LECIS)," Lab Automation '98 Conference, San Diego, CA, January 17–21, 1998 (contributed).

Staab, T., "The Development of the Laboratory Equipment Control Interface Specification," Computer Science Colloquium, Fachhochschule Wiesbaden, University of Applied Sciences, Wiesbaden, Germany, May 26, 1998 (invited).

Staab, T., "Instrument Interfacing Problems and Solutions," Lab Automation '98 Conference, San Diego, CA, January 17–21, 1998 (invited).

Patents

S.P. Layne and T.J. Beugelsdijk, "Method and Apparatus for Globally-Accessible Automated Testing," U.S. Patent No. 5,841,975 (November 24, 1998).

S. P. Layne, and T.J. Beugelsdijk, "Apparatus for Automated Testing of Biological Specimens," U.S. Patent Pending.

S. P. Layne, and T. J. Beugelsdijk, "Apparatus for Testing for Infection by a Retrovirus," U.S. Patent Pending.

S. P. Layne, and T. J. Beugelsdijk, "Mass Customized Testing and Manufacturing via the Internet," U.S. Patent Pending.

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The Milagro Project: Observing the Cosmos at Very High Energies

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Abstract

The Milagro gamma-ray observatory is a unique new detector being built by a collaboration of scientists from Los Alamos National Laboratory and nine universities, including the Universities of California at Irvine, Santa Cruz, and Riverside. Milagro uses the water-Cherenkov technique for the first time in an air-shower array to perform the first all-sky, high duty-factor observations in the 1-TeV (10^{12} eV, or about 10^7 times the energy of a typical x-ray) region. It is this ability to observe gamma rays coming from essentially anywhere in the overhead sky at anytime that makes Milagro unique in the world. Milagro was built in two stages, an initial prototype that operated for about a year (dubbed "Milagrito"), followed by installation of the complete detector.

Background

To describe the status of Milagro, a primary objective for the Milagro collaboration was to bring the initial prototype phase into operation in early 1997, well before the 1998 installation of the entire detector. The Milagrito phase of the detector was assembled during the fall of 1996 and brought into operation early in 1997. We made observations with Milagrito until April 1998, when the detector was turned off to allow installation of the full Milagro array. This prototype phase was remarkably successful, with the detector being operational over 85% of the time. We collected over nine billion air-shower events during that time and have used these data to produce some very interesting preliminary results (see below). Milagro is now completely installed, and final detector commissioning activities are now underway.

Progress

The Los Alamos group hosts the Milagro gamma-ray observatory, which is located at a Laboratory site about 35 miles west of Los Alamos in the Jemez mountains. The Los Alamos group serves the collaboration with a wide variety of responsibilities, which include

- design and development of the software for Milagro data acquisition;
- construction and operation of the laser calibration system;
- design and development of the remote-control run system for Milagro;
- supervision of the operation of Milagrito;
- ES&H oversight, maintenance of site infrastructure, and hosting of visitors; and
- supervision of graduate students and postdoctoral fellows from collaborating campuses.

In addition, Los Alamos heads three separate working groups within the collaboration.

The UC Irvine group studied the nature of Milagrito events that failed some of our computer reconstruction algorithms. Understanding these events is important to learning the characteristic configurations of event triggers that may not be the air showers. A method for identifying triggers due to large-angle muons and single hadrons was developed. A procedure for studying the energy spectrum of single hadrons is under development. This study will be used to estimate the spectrum of high-energy protons in cosmic rays up to the knee of the cosmic-ray flux. One of the graduate students worked on calibration methods for converting time-over-threshold information to pulse height, using the calibration system to trigger the Milagrito array. The technique will be extended to calibration for Milagro. She is working on the problem of identifying possible signals from gamma-ray bursts from Milagrito data. Two other collaborators have been working on the implementation of an "outrigger array" to determine the core location of events whose cores lie outside Milagro. Eleven outrigger water-Cherenkov tanks were installed in December 1998.

The UC Santa Cruz group continued research that refines the use of neural network (NN) algorithms for the reconstruction of Milagro telescope data. In particular, one of the graduate students tuned up his "unsupervised" NN to separate incident gamma rays from the hadronic cosmic-ray background. For the simple case of vertical particles, he gets true positive identification of gamma-rays 82% of the time and false positive identification of hadrons as gamma rays 39% of the time. This leads to an improvement in significance of 30%, equivalent to a 70% increase in running time. Although encouraging, the initial conditions are too simple to apply this to real data. In addition, a postdoctoral researcher has been using a "supervised" NN to examine muon identification in the calorimeter layer of phototubes in Milagro and to reduce the cosmic-ray background. He finds that the NN technique works better than does the traditional method of cutting on data, though of course this may simply mean that the NN found more efficient or effective cuts. In his plan for an improved detector, the NN technique was examined for its ability to separate gamma rays from cosmic rays. His results in both areas will be presented at the AIHENP '99 Sixth International Workshop on Software and Neural Networks in Physics Research.

Members of the UC Riverside group participated actively in various areas. A postdoctoral researcher and two graduate students are stationed at Los Alamos full-time. The UC Riverside group has contributed significantly to the construction and operation of Milagrito, the processing of the data taken with Milagrito, and the physics analysis. In particular, the two graduate students are analyzing the Milagrito data for their Ph.D. dissertation work. The postdoctoral researcher has performed several analyses and is responsible for the so-called environmental monitoring system of Milagro, a system that keeps track of the condition of all major systems of Milagro so that their condition can be monitored by experimenters remotely. The group has also contributed to the installation and commissioning of the full Milagro detector, as well as to the development and implementation of the data acquisition and reduction software.

The first source that any air-shower array, like Milagro, tries to observe is not actually a source, but an "antisource." Cosmic rays impinge upon the earth from all directions. A small fraction of these strike the moon and are therefore intercepted before they arrive at the earth. This produces what is commonly known as the "moon shadow" in the cosmic-ray flux, producing a sink (or antisource) of cosmic rays near the moon. The moon shadow has been traditionally used to study the angular resolution of an air-shower observatory and to verify the directional pointing of the array. Cosmic rays in the TeV energy range, where Milagro is most sensitive, are very significantly deflected by the earth's magnetic field. This bending is observed in the data from Milagrito, where the shadow is seen displaced from the position of the moon by about 1 degree. The apparent position and shape of the observed shadow is under great scrutiny, as much can be learned about the performance of Milagro. In addition, if some cosmic rays are actually antiparticles, they will be bent by the same amount, but in the opposite direction. Careful analysis of the data in the opposite direction from the observed moon shadow will allow Milagro for the first time to place severe limits on the flux of antiparticles.

The EGRET satellite detector has observed high-energy emission from a number of so-called blazars, distant galaxies that are thought to contain supermassive (10^6 to 10^8 times the sun's mass) black holes at their center. Three of the closest blazars have also been detected by air-Cherenkov telescopes in the 1-TeV region. We have preliminary results on one of these, the one known as Markarian 501, in data collected with Milagrito. This observation is the very first detection of an established gamma-ray source by an air-shower array. Results are now being analyzed for variability on many different time scales, as is expected of these sources, and will be the topic of a Ph.D. thesis.

Solar energetic particles from the solar flare of November 6, 1997, with energies exceeding 10 GeV have also been detected by Milagrito. Although particle acceleration beyond 1 GeV at the sun is well established, few data exist for protons or ions beyond 10 GeV. The Milagro observatory can also be used to study particle acceleration to extreme energies by the sun by making observations in a slightly different mode than normal. Milagrito was sensitive to solar proton and neutron fluxes above about 5 to 10 GeV. Milagrito operated in a scaler mode as well during its run, which was primarily sensitive to muons, low-energy photons, and electrons, and in the normal mode in which the detector is sensitive to showers and high zenith-angle muons. In its scaler mode, Milagrito registered a rate increase coincident with the November 6, 1997, ground-level event observed by Climax and other neutron monitors. This detection indicates the presence of >10-GeV particles (early analyses indicate a lower limit on the energies of more like >100 GeV), perhaps the highest-energy particles ever detected from the sun.

Further contributions by the Milagro collaboration include ten separate talks presented at the Twenty-fifth International Cosmic Ray Conference in Rome in 1997.

Frontiers of Materials Science Program: Overview

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Abstract

The aim of this program is to explore frontier areas of interdisciplinary materials science of common scientific and strategic interest to Los Alamos National Laboratory and the National Science Foundation's Materials Research Laboratory at UC Santa Barbara (UCSB). This aim is achieved through (a) minigrants, awarded competitively, to support specific projects involving graduate students or postdoctoral fellows with mentors at both institutions and (b) travel funds to support short visits to the Frontiers in Materials Science Seminar Series, topical workshops, and new project exploration. The interdisciplinary character of materials science at UCSB and Los Alamos and their complementary skills and facilities enable exploration of exciting new frontiers of materials science with maximal efficiency and flexibility, so that fields can be rapidly assessed for their technology and growth potential and competencies can be seeded. The excellent educational outreach initiatives at the Materials Research Laboratory, combined with the unique research environment at Los Alamos, provide special opportunities for training young researchers in interdisciplinary materials science.

The projects initiated to date include topics in areas of nonlinear-nonequilibrium multiscale processes, inorganic-organic interfaces, biomimetic materials, active thin films, complex fluids and soft condensed matter, magnetoresistive materials, neutron scattering, and molecular sieves.
New partnerships between numerous Los Alamos divisions and UCSB departments are represented. Workshops have been held at both Los Alamos and UCSB. The seminar series has been extremely popular with the Los Alamos staff and has generated enthusiastic pursuit of joint programs for the study of, for example, organic-inorganic hybrid materials. This is of great importance to rational strategies for understanding, controlling, and using complexity in electronic and structural materials—with profound impact on classes of materials lying between traditional disciplines of chemistry, solid-state physics, materials science, biological science, and geoscience. Likewise, the Frontiers of Materials Science Program has provided a clear impetus for Los Alamos involvement in DOE initiatives on complexity in materials science.

Background

The aim of this program is to explore frontier areas of materials science jointly between the National Science Foundation (NSF) Materials Science and Engineering Center (MRSEC), also known as the Materials Research Laboratory, at UC Santa Barbara (UCSB) and the materials science community at Los Alamos National Laboratory. This is achieved through minigrants and travel funds.

Minigrants support UCSB and Los Alamos graduate students or postdoctoral fellows who spend periods of time at both institutions with mentors at both. Individual grants are a maximum of approximately $50,000 per year (including cost sharing where appropriate), and the grants are subject to renewal on the basis of satisfactory performance and other considerations. Calls for proposals are made every six to nine months with the intent of securing a constant rolling level of effort. Each call is distributed widely at both Los Alamos and UCSB. Selection is made by a steering committee composed of Los Alamos and UCSB staff members.

Travel funds support short visits to either institution to facilitate seminars, on-going project discussions, exploration of new projects, and participation in topical workshops.

The MRSEC at UCSB was established in 1992 and was very favorably reviewed in 1996 and 1998; it is now one of the largest of the NSF MRSECs. It recently inaugurated a permanent building on the UCSB campus. It has displayed national leadership with a distinctive character of interdisciplinary materials research, with representation from more than 10 departments, including more than 40 faculty members and more than 60 research students and postdoctoral fellows. It has established innovative programs with local schools, and extensive national and international collaborations, including academic and industrial institutions. The relationship of the MRSEC with Los Alamos originates from its inception when Los Alamos gave strong support, which has continued through membership on the External Advisory Board at UCSB.

Materials science is a relatively young departmental discipline at UCSB with the advantage that interdisciplinary activities between departments have been directly encouraged and facilitated. This relative freedom from discipline boundaries matches the research style at Los Alamos extremely well and allows exploration of frontier materials science topics of unusual complexity. It was therefore appropriate that the two institutions should partner through the current program to explore selected new topics of mutual interest and benefit with maximum efficiency and flexibility. The partnership brings many benefits:

- building on existing professional contacts to define and advance frontier materials areas;
- using the excellence of industrial outreach at the MRSEC to explore collaborations or agency initiatives;
- combining the advantage of the excellent student, postdoctoral, and educational outreach programs at UCSB with the opportunity to broaden the education of young researchers in the unique Los Alamos research environment and to broaden their job opportunities; and
- using complementary facilities and skills at the two institutions, including national user facilities and specialized equipment.

The broad materials competency aims at Los Alamos, which match the UCSB MRSEC so well, are the understanding and control of synthesis-structure-property relations in complex electronic and structural materials, particularly in new classes of materials lying between traditional solid-state physics, chemistry, metallurgy, biology and geosciences—in short, the measuring and modeling of multiscale nonlinear and nonequilibrium processes so as to understand, control, and use intrinsic complexity for existing and emerging technologies.

The four major research thrusts in the MRSEC are the following: complex fluids, solution synthesis of inorganics at molecular and atomic interfaces, heterogeneous polymeric structures, and strongly nonequilibrium phenomena in complex materials. These thrusts resonate very strongly with many Los Alamos divisions and program offices and with Laboratory-Directed Research and Development (LDRD) thrust directions. They also complement several program directions, including polymers, sensors, thin films, molecularly engineered and nanostructural materials, biomimetic materials, fracture and friction, multiscale science, etc., and are exciting science areas for use of our major facilities, including neutron scattering, high magnetic fields, ultrafast spectroscopy, and large-scale simulations.

Progress

The first year began in February 1997 with the first call for minigrants. Subsequent calls were announced at Los Alamos and UCSB in August 1997 and June 1998. In view of uncertainties in UCDRD funding for FY 2000, the last call was more limited in nature. The calls focused on the following topics, chosen to optimize relevance to the goals of both Los Alamos and UCSB:

- Nonlinear-Nonequilibrium Materials Processes
- Inorganic-Organic Interfaces and Biomimetic Materials
- Active Thin Films
- Complex Fluids and Soft Condensed Matter
- Magnetoresistive Materials
- Neutron Scattering Studies of Materials
- Molecular Sieves for Separation or Catalytic Applications

Proposals were received from eight divisions at Los Alamos. They were reviewed jointly at Los Alamos and UCSB, and the following projects were chosen through the three calls:

- Investigation of Electronic Transport through Organic Self-Assembled Monolayers Using Ballistic Electron Emission Microscopy
- Study of Island Growth Mode of Epitaxy and Phase Selection of Perovskite Thin Films by Solution Methods
- Giant Magnetoresistance in Metal Oxides
- Macroscopic Ordering of Silicate Surfactant Mesophases by Electrophoresis
- Theoretical Studies of Thermally-Induced Failure of Polycrystalline Metallic Films
- Neutron Scattering and Vibrational Probes of Structure in Layered Perovskite CMR Materials
- Molecular Density and Orientation in Confined Polymer Layers under Static and Dynamic Conditions
- Electrostatic Interactions in Biomaterials
- Extending the Scale of Self-Assembly to Macroscopic Dimensions: Oriented Fluorescent Microwires and Biosensors

The proposals were chosen on the basis of technical quality, qualifications of the principal investigators, benefit to Los Alamos and UCSB existing programs and potential for growth, and reasonableness of budget for proposed work. Each of the proposals included explicit postdoctoral or student involvement. The variety of matching funds from agency grants and industry was extremely impressive. Reports on the current projects are provided individually.

In addition to the minigrants, 10 small visiting budgets have been approved to enable project exploration. Also three workshops have been partially funded: "Thin Films" (held at UCSB in 1997); "Texture, Stress, and Microstructures" (held at Los Alamos in conjunction with Los Alamos Neutron Science Center programs, 1998); and "Self-Assembling and Biomimetic Materials" (held at Los Alamos in conjunction with the Center for Materials Science and the Center for Nonlinear Studies, 1998).

Of special note is the enthusiasm, at both institutions, with which the UCSB and Los Alamos Frontiers of Materials Science Seminar Series has been received. This series has been organized by Los Alamos staff members and has found striking support from researchers in multiple divisions—such as the Chemical Science and Technology (CST) Division, the Materials Science and Technology (MST) Division, the Life Sciences (LS) Division, and the Theoretical (T) Division—and centers, including the Center for Materials Science, the Center for Nonlinear Studies, and the Manuel Lujan Jr. Neutron Scattering Center. Equally encouraging is the response of science managers at Los Alamos and UCSB to explore steps to formalize and extend a joint research program, possibly as an explicit MRSEC thrust.

The seminar series has facilitated short visits to Los Alamos by key members of the UCSB Materials Research Laboratory (MRL). These visits have been designed with several goals in mind: (a) to foster collaborative interactions between the materials science community at Los Alamos and the UCSB MRL, with special emphasis on the area of complex materials, which is taken to include molecularly engineered materials, biomimetic materials, soft condensed matter, materials with large nonlinear responses, self-assembling systems, and materials whose properties are controlled in a rational manner by design of hierarchical levels of structures; (b) to facilitate interactions with the high-level seminar speakers to help define specific research topics in this emerging area that are important to Los Alamos and in which Los Alamos is positioned to make a major scientific impact; and (c) to help identify a strategy for unifying the diverse efforts at Los Alamos that comprise our already existing programs within this overall area of materials research.

There have been multiple presentations by MRL speakers at UCSB, who represented numerous organizations, including the Materials Research Laboratory, the College of Computer and Electronic Engineering, the Organic Polymer Institute, and the following departments: Chemistry; Molecular, Cellular, and Development Biology; Physics; Materials; Chemical Engineering; and Environmental Engineering. In all cases, the visit included a seminar presentation, a round-table discussion focusing on strategies for developing UCSB and Los Alamos collaborations, and a number of meetings of the speaker with individuals or small groups of Los Alamos staff and with senior Los Alamos managers. Although the research interests of the speakers are diverse—with specific topics including understanding of electrostatic interactions in polymers, control and characterization of electronic properties of semiconductors, thin-film growth and morphology, synthesis of novel zeolites based on control of chemistry at the organic/inorganic interface, and understanding the synthesis of novel materials by biological organisms—several underlying and unifying scientific themes have emerged from these visits.

One theme is that a detailed understanding of molecular-level and mesoscale interactions, including complex electrostatic forces and nonlinear and nonequilibrium processes, is required for the rational control of macroscopic materials properties. This type of materials research requires theoretical and experimental tools just being developed, but already there have been many surprises. For example, discussed in some detail were (a) how even the sign (attractive or repulsive) of the electrostatic forces between like-charged groups in complex polymers is not understood and (b) the importance of electrostatic interactions in understanding the heat of adsorption versus loading for chlorinated hydrocarbons in different zeolites. Further, all of the presentations emphasized that a combined experimental and theoretical approach is required to successfully examine these types of problems.

Another clear theme that has emerged is the importance of understanding the assembly of mesoscale building blocks into macroscopic materials. Often this type of assembly involves control of interactions at the interface of two fundamentally different types of substances, such as an organic/inorganic interface or an inorganic/biological interface. For example, materials synthesized by natural systems and how biological materials synthesis can control macroscopic features by control of properties of a microscopic organic/inorganic interface were described. Obviously, such work requires input from a number of different traditional disciplines and is thus highly interdisciplinary in nature. A powerful presentation was given on the opportunities for combining biological, chemical, and physics resources to address biomimetic and bio-inspired materials synthesis. This has stimulated new collaborations at Los Alamos on templating and guest-host organic-inorganic structures with new electronic, optical, and mechanical properties.

The round-table discussions served both to further focus these general scientific themes and to explore strategies for development of a unified Los Alamos effort, including possible collaborations with UCSB. One important topic of discussion was the motivation for rapidly growing areas of research. A general conclusion was that the thinking embodied in the rational design or molecular engineering of material properties is a fundamentally new way to think about the control of these properties and that the long-term impact of this approach is just beginning to be evident. Even so, there are already many important applications emerging. These include (a) the control of electrostatic properties to assist in the development of aqueous based material processing, cost effective in terms of both starting materials and environmental impact; (b) the use of well-characterized soft condensed matter or self-assembled systems as model systems for the study of traditional materials science issues such as defect formation, crystal growth, fracture and stress dynamics; (c) the ability to tune the structure and properties of materials by rational kinetic control of their synthesis, much in the same manner used by many biological organisms for material growth; and (d) the design of materials with multiple hierarchical levels of structures that interact to facilitate a particular function. Specific applications relevant to Los Alamos efforts include sensors, advanced separation technology, catalytic systems, and electronic and optical device construction.

The organization of interdiscplinary efforts in complex materials was also discussed at length. One theme that emerged from these discussions is that individual programs in this general area already exist at Los Alamos but suffer from a lack of visibility and funding opportunities related to the lack of a clearly defined institutional home. In turn, this lack of an institutional home is linked to the highly interdisciplinary nature of the work, an issue also faced by UCSB in the development of its MRSEC. A general agreement was reached that a clear and concise statement of purpose and description of how research programs in this area relate to desired Los Alamos laboratory competencies is needed. An interdisciplinary informal working group with active representation from staff members in CST, MST, T, and LS Divisions evolved to begin to address this need, leading to the institutional grassroots efforts in Complex Adaptive Matter (see below).

Other specific issues have been raised by the UCSB visitors during the round-table discussions about the role of Los Alamos in this type of materials research. One important point is the existence of state-of-the-art materials characterization capabilities at Los Alamos and the role to which these already existing capabilities can help nucleate an interdisciplinary program. In addition, the advanced modeling and theoretical capabilities at Los Alamos were seen as an enormous strength. One intriguing specific idea was to establish a direct link between research at Los Alamos and UCSB by development of a joint thrust (the MRSEC at UCSB currently is organized into four such thrusts, previously mentioned), primarily focused on exploration of the interfaces of organic and inorganic materials.

Reciprocal seminar visits by Los Alamos staff members were organized by the UCSB MRL and advertised at UCSB as the Frontiers in Material Science Series. During FY 1998 and FY 1999, senior Los Alamos researchers spoke at the seminars, spent extended change-of-station periods at UCSB to pursue joint research projects, and gave graduate lecture courses. One staff member spent three months at the Institute for Theoretical Physics at UCSB, where he participated in an extended workshop organized by a UCSB colleague in the present program. Another is an active member of the UCSB MRL External Advisory Committee. Still another researcher has moved from a postdoctoral position at Los Alamos to a faculty position in chemistry at UCSB. Los Alamos funding through this Frontiers program is given high visibility in the MRL presentations and reviews.

The excitement and stimulation of new ideas at the frontiers of materials science originated by the collaborations with UCSB through the present program are evident in a number of recent key developments. An example is an opportunity for joint programs with UCSB and Los Alamos staff to study active thin films as part of the National Semiconductor Research Corporation programs. Most striking is the acceptance that controlling and using complexity is the paramount frontier for interdisciplinary materials science. This is clear from the grassroots enthusiasm at Los Alamos for projects in Complex Adaptive Matter in FY 1998 and FY 1999, leading to several novel LDRD DR and ER projects, and most recently to the notion of a national Institute for Complex Adaptive Matter centered at Los Alamos, with enthusiastic support from the UC Office of the President. This direction is further recognized by a newly announced program by DOE-OS on Complex and Collective Phenomena. The UCDRD-sponsored collaborations with UCSB through the present program have placed Los Alamos staff in an especially advantageous position to compete (and indeed to lead) in this new DOE direction. The excitement and reality at Los Alamos is now very strong for seeking interdisciplinary research projects between hard, soft, and biological matter; between organic and inorganic; and between solid-state, materials science, chemistry, and biology. The last three years have changed the atmosphere qualitatively. Indeed, several joint proposals between UCSB and Los Alamos staff are being prepared for the new DOE, and related, calls.

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Frontiers of Materials Science Program: Macroscopic Ordering of Silicate-Surfactant Mesophases by Electrophoresis

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Abstract

There is increasing interest in the preparation of highly ordered composite materials with novel mechanical, optical, magnetic, electronic, and/or catalytic properties, which are organized over a hierarchy of lengths scales. In nature, highly regular mineralized microlaminate composites are formed through the concerted action of mechanisms that direct the organization of inorganic and organic structures over a large range of different length scales. This is not easily done using conventional synthesis techniques. Therefore, we have explored strategies to create nano- to macro-scale structural order in new synthetic composite materials by combining (a) our well-developed capabilities for controlling nano- and meso-scale ordering of organic molecules (surfactant) with inorganic species (silicates and analogs) with (b) the macroscopic structural ordering/patterning that has been demonstrated in certain systems where diffusion and reaction are balanced. This project has focused on developing the fundamental methodologies and conditions by which macroscopic ordering of technologically promising inorganic-organic composites and porous solids can be produced through the application of electromagnetic fields.

With support from the UCDRD program, we have (a) measured, for the first time, pulsed-field gradient (PFG) nuclear magnetic resonance (NMR) diffusivities of monomeric and double four-membered ring silicate anions in aqueous solution and in gels; (b) correlated electrical conductivity measurements with PFG NMR results to assess ion-pairing interactions in solution; (c) demonstrated that aqueous silicate solution equilibria under highly alkaline conditions are not perturbed by incorporation in an agarose gel; and (d) developed capabilities in electrophoresis nuclear magnetic resonance spectroscopy for in situ solution-phase ^{229}Si NMR studies of silicate and surfactant solutions in the presence of electric fields. These results are central to the development of electrophoretic processing strategies that regulate diffusion and reaction to control patterning of mesostructurally ordered inorganic-organic composite materials.

Background

Novel synthetic composite materials that mimic the properties of certain biological composite materials show promise in the areas of protein and large-molecule separations, robust and selectively permeable coatings, catalysts, semiconductors and photonics, energy storage, and specialized construction materials with high anisotropy and strength-to-weight ratios.
A significant amount of work has been done

in the field of biomimetics to elucidate the way nature forms such materials with highly ordered, patterned structures.

For example, the shell of the abalone is an inorganic-protein composite displaying structural order from molecular to macroscopic dimensions. At the molecular level, the phase and orientation of calcium carbonate is determined by specific protein-inorganic interactions. At the nanometer-length scale, the offset of crystalline aragonite tablets is determined by the distribution of pores in interlamellar protein sheets. At the millimeter-length scale, genetic determinants create repeating organic sheet/calcite/aragonite units, which are organized into a shell architecture over centimeter-length scales. The result is an extremely strong micro-laminate composite. The creation of such structures is based upon dynamic spatial and/or temporal control of assembly, achieved though a delicate balance of a combination of forces and processes operative over different length scales, including hydrodynamic or viscous forces arising from nonequilibrium conditions.

Other examples are the intricately colored patterns found in many molluscan shells and tropical reef fish. These are believed to be produced by the creation of standing waves of products and reactants controlled by Turing reaction mechanisms. Spatially and temporally varying species concentrations are generated via delicately tuned nonequilibrium reaction-diffusion systems composed of highly selective enzyme-catalyzed reactions and diffusion regulation across membranes at intracellular, intercellular, and macroscopic-length scales.

Based on current understanding, the development of "one-shot" synthesis strategies capable of mimicking these complicated processes employed in nature will be exceedingly difficult to find. For this reason, our approach to the production of synthetic composite materials, particularly in the context of this minigrant proposal, seeks to engineer key nonequilibrium synthesis procedures in order to create similar patterned material structures. This approach will use UC Santa Barbara (UCSB) expertise in the area of molecular and mesoscopic self-assembly of inorganic (silicates and analogs) and organic (surfactants, peptides, and proteins) species in aqueous solution and Los Alamos National Laboratory expertise in the area of electrolyte chemistry and electrophoresis.

Progress

Technical Approach. The focus of this joint UCSB-Los Alamos effort has been use of our complementary tools and perspectives to control molecular and mesoscopic inorganic-organic material structures over macroscopic-length scales. The UCSB group has recently demonstrated the rich liquid crystalline chemistry and physics underlying the preparation of mesostructured inorganic-surfactant materials using low-molecular-weight amphiphiles.[1,2] Furthermore, high degrees of orientational order can be produced in both the lamellar and hexagonal silicate-surfactant mesophase systems in the presence of a strong magnetic field.[3,4] Various surfactants and conditions can be used, which lead to different mesophase structures and compositions,[5] though typically not via thermodynamically stable liquid crystalline intermediates. In particular, the types of silicate species (or other polymerizable inorganic precursor) available for coordination with the surfactant are strongly dependent upon the pH of the solution, the base cation (e.g., alkali metal or tetra-alkylammonium species), silicon-to-hydroxide ratio, temperature, and the concentration of alcohol additives or hydrolysis products. For example, in the presence of tetramethylammonium hydroxide (pH = 12.5) and methanol, the predominant silicate species is the double four-membered ring (D4R) anion, which is key for forming stable silicate-surfactant liquid crystals that can be processed.[1,2]

The presence of charged inorganic and surfactant species in mesostructured materials syntheses is important in that their interactions with electric fields may allow the preparation of patterned structures. One processing strategy to achieve involves the use an electric field to regulate the diffusivities of charged inorganic and organic molecular species, permitting their rate of mass transport to a reacting interface to be thereby controlled. To implement this in practice, it is necessary to know the relative mobilities of the various charged silicate and surfactant solution species, as functions of solution conditions (especially pH) and electric field strength, which must be optimized accordingly. An important goal of our efforts has consequently been the determination of the diffusivity and mean charge of different precursor silicate anions, which have been measured by means of a combination of pulsed field gradient (PFG) diffusion and electrophoresis nuclear magnetic resonance (ENMR) techniques and bulk conductivity measurements.

Capabilities at UCSB and Los Alamos. The Los Alamos electrophoresis/pulsed-field gradient nuclear magnetic resonance (NMR) equipment consists of multi-nuclear PFG NMR probe heads (tunable over a broad frequency range) with a modular electrophoresis cell. The PFG system is capable of gradient strengths up to 40 G/cm, whereas the electrophoresis cell operates at currents between 20 and 100 mA. An additional probe is rated to 800 G/cm for 5% duty cycles and can achieve 200 G/cm for more frequent gradient pulses. The gradient strength directly translates into higher spatial resolution, over which ion mobilities can be detected. The system can operate at temperatures between –50°C and 100°C with a temperature stability of ±0.5°C. The capabilities of this system for quantifying ion mobilities in aqueous polymer gel electrolytes have been well documented[6] and have been extended to allow studies on many different types of samples.

Of special relevance for this work, Los Alamos is the only laboratory actively pursuing studies in liquids. Because of convection and other problems, the three other laboratories in the world with ENMR capability have always used gelled electrolytes. Our combination of NMR and electrochemical expertise provides opportunities for examining either solution or gel samples containing silicate and/or surfactant species. Finally, insight into problems, such as current distributions in ENMR cells, is available at Los Alamos, where electrochemical systems have been intensively studied.

As discussed above, the groups at UCSB are international leaders in the synthesis and processing of inorganic-surfactant mesophase materials. This also includes unique characterization capabilities, including ^{2}H, ^{13}C, and ^{29}Si NMR, two-dimensional heteronuclear correlation NMR spectroscopy, x-ray diffraction, infrared/Raman spectroscopy, scanning and transmission electron microscopy, and atomic force microscopy.

Progress to Date. The project's two graduate students in the UCSB Department of Chemical Engineering have worked at Los Alamos with the Laboratory investigator. In 1998 the Los Alamos investigator spent several months engaged in research and teaching in the Department of Chemical Engineering at UCSB. The campus investigator visited Los Alamos in September 1998 for research discussions.

To date, we have measured self-diffusion coefficients for D4R and monomeric silicate anions in highly alkaline aqueous solutions in the absence of an applied electric field. The few published studies of silicate anion diffusion in alkaline solutions have been produced under conditions where a number of different silicate species are in rapid chemical exchange with each other. We have succeeded in measuring separately the mobilities of the monomeric $(SiO_4H_{4-x})^{x-}$ and D4R $(Si_8O_{16}H_{8-x})^{x-}$ anions under highly alkaline conditions, where these are the dominant or only detectable silicate species present. (In ethanol-stabilized monomer solutions, small concentrations of silicate dimers and cyclic trimers were present and accounted for, whereas only the D4R species were present in methanol-stabilized solutions.) The D4R species possess a self-diffusion coefficient at 25°C that is roughly half that of the monomer ($D_{D4R} = 2.9 \times 10^{-6}$ cm^2/s vs $D_{mono} = 25.7 \times 10^{-6}$ cm^2/s, both of which are substantially smaller than for pure water $D_{water} = 2.2 \times 10^{-5}$ cm^2/s). These results are consistent with the higher-charge, larger molecular size/ionic radii, and higher solution viscosity for these species and their solutions in comparison with water. The results are also consistent with separate solution-state conductivity measurements, which additionally indicate significant ion-pairing between the D4R anions and tetramethylammonium cations and/or associated water molecules. This work is currently being pre-pared for submittal to the journal *Langmuir.*[7] It has yielded key understanding and insights that are being applied now to electrophoretic mobility studies of silicate-surfactant systems.

ENMR measurements are currently in progress to examine the regulatory effects of an electric field on the diffusion of charged silica species in aqueous solutions at high pH. In general, precise quantitative measurements of electrophoretic mobilities in liquids are difficult, because of the potential for sample heating by the applied electric fields or the evolution of gas bubbles at the electrodes, both of which can lead to undesirable convection currents. These problems can be alleviated by measuring diffusion in viscous gels instead of liquids. To this end, we have determined on the basis of solution-state ^{29}Si NMR experiments that equilibrium silicate anion speciation, particularly that associated with the D4R species, is not affected by casting the solution into a 1 wt% agarose gel. PFG NMR measurements on this system show, however, that the D4R self-diffusion coefficient decreases by a factor of three ($D_{D4R} = 7.6 \times 10^{-7}$ cm^2/s), indicating that the gel acts as a physical obstruction, but does not interact chemically with the silicate species to a significant extent.

To obtain sufficient signal sensitivity, such studies must be done using 100% enrichment in ^{29}Si, the NMR-active isotope silicon (about $100/mg in the form of $^{29}SiO_2$). We have developed the necessary experimental equipment and procedures for conducting such measurements in a feasible and cost-efficient manner. This has entailed constructing ENMR sample cells of reduced volume (1- to 2-ml, as opposed to 4- to 6-ml conventional cells) and using rapid NMR pulsing techniques (DEFT, for driven-equilibrium Fourier transformation) to provide faster signal averaging.

In addition, we have established the design and materials criteria for the ENMR electrode, which is being fabricated out of hydrided palladium. Our preliminary and current results are being analyzed on the basis of existing theoretical models to establish the self-diffusion coefficients and mean charges of the monomeric and D4R silicate species under the conditions of liquid crystal self-assembly. Such quantitative data have never been measured. These results are necessary for selecting the conditions under which regulatory control of diffusion, self-assembly, and polymerization of silicate-surfactant liquid crystal systems can be achieved to reach our broader patterning objectives. These experiments will be ongoing between UCSB and Los Alamos and are expected to lead to additional publications.

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Presentation

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Frontiers of Materials Science Program: Electrostatic Effects in Biomaterials

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Abstract

Several new materials applications attempt to take advantage of the ability of nature to self-assemble complex structures with well-defined functionality/property and thereby create a completely new class of adaptive material composites with novel applications. Examples are (a) self-assembled single or multiple layers for coating, interfaces, and electrooptic purposes and for making surfaces with specific sensor abilities for recognizing chemical or biological toxins; (b) cationic liposomes complexed with DNA as synthetically based nonviral carriers (or storage) of DNA vectors (e.g., for gene therapy); and (c) peptide oligomer structures for holographic data storage. Since such applications attempt to mimic biological processes, a further advantage is that the materials processing (manufacturing and destruction) can be performed in water solutions, which are both inexpensive and environmentally benign.

The solubility of macromolecules in aqueous media is controlled by the ionization of polar species and/

or hydrogen bonding to the water molecules. This proposal focuses on the electrostatic interactions between macroions and microions in aqueous solutions, which are key to many biological processes and are linked to the hydrophobic/hydrophilic properties of the molecular structure of charged groups of the molecules. However, little is known about electrostatic interactions in molecular complexes where macromolecules of similar or opposite charges interact through the presence of microions (salt) of various kinds. The principal existing theoretical approach is based on mean-field (Poisson-Boltzmann) type approximations for the salt distributions around macromolecules, but results of such formalisms have proved to be inadequate in many physical situations.

The purpose of the proposed work is to investigate the complexity of electrostatic interactions theoretically through controlled model systems. The specific aim is to identify the key electrostatic parameters necessary for successful manipulation of biomaterials. Experimentally, such parameters are typically salt concentration and salt type, pH, and sometimes temperature.

This proposal and the work conducted have seeded several new experimental/theoretical collaborations between Los Alamos National Laboratory and UC Santa Barbara, as well as within the Laboratory. The main reason for this is that we did not previously have a direct theoretical framework for mediating experimental experiences between Los Alamos and UC Santa Barbara.

The past year has produced the first simulations demonstrating effective attractive interactions between like-charged spherical colloids in divalent counterion solution. We have performed simulations of adhesion of stiff polyelectrolytes onto charged surfaces and compared the results to experimental x-ray data from Los Alamos. We have further developed the polyelectolyte adhesion work in the form of a theoretical framework for explaining the adhesion force when the surface is oppositely charged to the polyelectrolytes and when the charge densities are relatively low. We have investigated the effective interactions between polyelectrolytes and a polarizable surface and compared simulations to mean-field theory.

Refereed Publications

Grønbech-Jensen, Niels, Keith M. Beardmore, and Philip Pincus, "Interactions between Charged Spheres in Divalent Counterion Solution," *Physica A* **261**, 74 (1998).

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Presentations

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Grønbech-Jensen, Niels, "Effective Interactions between Solvated Macromolecules," CPiP '98, The University of the West Indies, Cave Hill, Bridgetown, Barbados, January 7–10, 1998 (invited).

Grønbech-Jensen, Niels, "Electrostatic Effects in Soft Condensed Matter," Risø National Laboratory, Roskilde, Denmark, May 1998 (invited).

Grønbech-Jensen, Niels, "Simulations of Interacting Charged Objects," Centennial Meeting of The American Physical Society, Atlanta, GA, March 20–26, 1999 (invited).

Workshop Participation

Grønbech-Jensen, Niels, Workshop on Electrostatic Effects in Complex Fluids and Biophysics, Institute for Theoretical Physics, Santa Barbara, CA, August 10–December 18, 1998 (invited).

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Frontiers of Materials Science Program: Neutron Scattering and Vibrational Probes of Structure in Layered and Perovskite CMR Materials

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Abstract

Complex advanced materials are finding new technological applications in areas such as superconductivity and magnetoresitance. These materials are finding new applications in high-density memory storage and novel electronic architectures. In these materials, transport properties are modulated by three-dimensional coherence and competition between electron-electron (el-el) and electron-phonon (el-ph) coupling. The close interplay among charge, spin, and lattice degrees of freedom is believed to play an important role in the mechanism of transport in itinerant ferromagnets. In the layered compounds $La_{2-2x}Sr_{1+2x}Mn_2O_7$, the

large extend interaction between spin, charge, and lattice correlates with ferromagnetism, antiferromagnetism, charge ordering, a metal insulator transition and colossal magnetoresistance (CMR). Although a great number of investigations have resulted in the understanding of the mechanism of magnetic and electronic coupling and the structural response, the significance of lattice dynamics on the interpretation of the CMR effect is still limited. We have correlated the vibrational, structural, and theoretical properties of the layered perovskite $La_{2-2x}Sr_{1+2x}Mn_2O_7$, allowing the opportunity to explore the relationship between structure and transport properties on varying length and time scales. Through this collaborative effort, we probed the polaronic nature of these materials in magnetic fields in order to elucidate the length scale and/or hopping frequency of polarons below Tc.

During the past two years, we have continued a concerted theoretical and structural study of the changes at Tc in CMR lanthanum-based manganites, $ABMn_2O_7$ (A = La, B = La, Sr, Ca). The research has focused on correlation of the temperature-dependent neutron structural data, resonance Raman and inelastic neutron scattering of $La_{1.2}Sr_{1.8}Mn_2O_7$, $LaSr_2Mn_2O_7$, $Sr_3Mn_2O_7$, and MnO_2. Recent temperature-dependent Raman and inelastic neutron scattering/spectroscopy on the layered CMR manganites reveals (a) the presence of charge-density wave behavior above Tc, (b) slow dynamic hopping, (c) Mn(II) in the lattice, and (c) local polarons. The research funded through UC–Los Alamos joint funding has produced 12 invited papers in symposia specifically on magnetoresistance. Two manuscripts have been submitted to *Physical Review B*, and based on the collaborative work two more manuscripts will be submitted in the next six months. The research has opened new avenues for university collaborations and inter-laboratory funding (Los Alamos and Argonne National Laboratory), which we are currently pursuing.

Refereed Publications

Argyriou, D.N., H.N. Bordallo, J.F. Mitchell, J.D. Jorgensen, and G.F. Strouse, "Lattice Displacements above Tc in the Layered Manganite $La_{1.2}Sr_{1.8}Mn_2O_7$" (submitted to *Phys. Rev. B*).

Bordallo, H.N., G.F. Strouse, J. Eckert, and J. Gardner, "Analysis of the Lattice Modes of Vibrations by Raman Spectroscopy and Inelastic Neutron Scattering in the Layered CMR $La_{2-2x}Sr_{1+2x8}Mn_2O_7$" (submitted to *Phys. Rev B*).

Presentations

Argyriou, D.N., H.N. Bordallo, and G.F. Strouse, " Spin-Charge-Lattice Coupling in Reduced Dimensions" University of California, Santa Barbara, CA, February 1999 (invited).

Bordallo, H.N., "Raman Scattering in Layered Colossal-Resistance Materials," New Mexico State University, Las Cruces, NM, November 1997 (invited).

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Frontiers of Materials Science Program: Molecular Density and Orientation in Confined Polymer Layers under Static and Dynamic (Flow) Conditions

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Abstract

Polymer molecules at solid or fluid interfaces have an enormous spectrum of applications in a wide variety of technologies. They provide a mechanism to impart colloid stabilization; they are used as protective coatings (including mechanical protection of solids against friction and wear); they govern the interactions of biological cell surfaces; and through judicious design, they are used to modulate dispersion properties (such as rheology) under a variety of processing conditions. Knowledge of the conformations that adsorbed or terminally anchored chain molecules adopt when subjected to confinement and/or solvent flow near surfaces is essential for predicting the interaction forces and rheological properties of the polymer layers involved in all of the above applications.

There exists a substantial body of theoretical literature and experimental data on the static morphologies of adsorbed polymers, grafted chains, block copolymers on surfaces, etc. For the most part, however, dynamic behavior under shear has only been inferred from techniques such as ellipsometry, where the mean hydrodynamic thickness of the polymer layer is measured optically, or the hydrodynamic flow method, where the increased resistance to flow due to the surface-bound polymer layer is measured, again providing an indication of the polymer layer thickness. Although those two techniques enable average polymer layer thicknesses to be evaluated, they do not provide any information on the seg-mental conformation or density profile of the polymer chains. Even less known is the effect of geometric confinement imposed by a second surface on polymer conformation, although this more closely matches the conditions of colloidal processing and the many other technological situations listed above.

Attempts to explain the interaction between surface-bound polymer and solvent flow have progressively evolved from theoretical treatments. The largest obstacle in the continuation of our understanding of such systems is precise experimental data, specifically the polymer segment density profile away from a surface under confinement or into a flowing solvent (or opposing polymer) layer. The aim of our study is to measure (a) molecular orientations and density distributions of physically adsorbed and chemically grafted polymer chains on solid supports; (b) how these are affected by shear at a single surface; and (c) how the proximity of a second surface (imposed confinement) alters the conformation, intersurface forces, and rheology of polymer layers in thin films.

To this end, we proposed a UCDRD project to construct a new apparatus for use in the SPEAR beam line that would enable the separation between two flat, macroscopic solid surfaces to be controlled and measured, as well as the normal and hydrostatic pressures while fluid is flowing between them. This has never been achieved before. The information obtained from these measurements will allow an assessment of how molecular orientations are dependent on confinement and flow and how the properties of complex fluids in thin films and narrow pores differ from bulk, for example, in mesoporous materials, during processing and lubricated sliding.

Toward the above goal, we have designed and built a new apparatus called the Neutron Flow Cell. This apparatus is capable of applying a known and controllable force in excess of 2000 lb upon two optically flat ($\lambda/30$) parallel plates (5 cm by 5 cm) using a removable hydraulic ram. The load is applied through a series of bevel springs, and once the desired plate separation or confined film thickness is obtained, the apparatus can be locked at this position. On the basis of preliminary studies, ultrathin gaps of 0.1 μm or less between the plates should be accessible. Another key feature of the new apparatus is that shear flow can be induced between the surfaces. To do this in a controlled manner and to ensure that fluid is flowing between the surfaces, we simply induce the shear by sliding the lower plate relative to the upper plate using a high precison micro-meter screw. A mechanical slider enables the lower plate to move while maintaining a constant applied force between the substrates.

The construction of the Neutron Flow Cell was completed in October 1998. The first experiments on the structure that complex fluids adopt under confinement and flow are scheduled for February 1999.

Presentation

Kuhl, T.L., J.N. Israelachvili, J. Majewski, and G. Smith, "Molecular Density and Orientation in Confined Polymer Layers: Coupling Direct Force Measurements with Neutron Scattering," Meeting of the Materials Research Society, Boston, MA, November 29–December 3, 1998 (contributed).

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Frontiers of Materials Science Program: Investigations of the Structures of Microtubule-Based Cellular Motors Using Neutron Scattering

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Abstract

Adenosine triphosphate (ATP) is the universal currency of chemical energy in biological systems. It is the fuel for muscle contraction, cell motility, biological pumps, and cellular "biomotors," which have diverse functions in biology. These functions range from organelle transport to segregation of chromosomes during meiosis and mitosis. The long-term goal of our research focuses on understanding how the chemical energy stored in ATP is converted into movement by cellular motors that move along microtubule (MT) tracks. In this first stage of our work, we are determining the low-resolution structure of the dimeric microtubule-based motors non-claret disjunctional (*ncd*) protein and kinesin when free in solution. As these motor domains contain the ATPase and MT binding sites, we can test to see whether there is a direct coupling with ATP hydrolysis to produce the large changes in structure required for movement. We are now searching for changes in the structure of free motors when nucleotide and nucleotide analogs, which are believed to represent important kinetic intermediates, are bound. In addition, we are examining the structure of the prominent rod portion of the kinesin motor to determine if it contains a flexible region. Eventually, we hope to determine the in situ structures of these motors when they are attached to microtubules with different nucleotides and nucleotide analogs present. We expect that the structures of free and bound motors will give insight into how the two-motor domains coordinate to produce motility.

We are studying an important basic science question about energy transduction in biology. In the long run the knowledge obtained may contribute to a further understanding of cancer and heart disease. In the short run we believe that this project will strengthen structural biology and the use of neutron scattering to investigate structural biology, at Los Alamos. As the Los Alamos Neutron Science Center (LANSCE) is just now becoming useful for biological studies, but has little experience in this area, our project will accelerate the ability of others to do such work at LANSCE by solving related physical and logistical problems. In addition, some of the projected work will require the implementation of a method recently proposed by the campus investigator. A successful implementation of this method, which may require significant experimental development, will allow it to be used for other biological problems and perhaps be adapted to neutron studies in other disciplines.

We have now determined the structures of these motors with ADP (the hydrolysis product of ATP) bound and find that the solution structure of *ncd* dimer has twofold symmetry about its rod axis and agrees well with the crystal structure. However, the structure of kinesin is more compact than that of the crystal structure—even though it retains the lack of twofold symmetry about the rod axis found in the kinesin crystal

structure. These results indicate that in vivo the differing directionality of movement of these two motors is due to the difference in their large-scale structures.

Publication

Stone, D.B., R.P. Hjelm Jr., and R.A. Mendelson, "The Solution Structures of Dimeric Kinesin and *Ncd* Motors" (to be published in *Biochemistry*).

Research and Education Utilizing the National High Magnetic Field Laboratory (NHMFL): Overview

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Abstract

The UCDRD funding for the National High Magnetic Field Laboratory (NHMFL) Project has been quite valuable for providing seed money to attract visitors from the University of California (UC) campuses whose research interests dovetail with the unique high-magnetic-field experimental capabilities offered by the NHMFL at Los Alamos National Laboratory. Since its inception in FY 1996, thirteen different principal investigators (PIs) from six UC campuses have been recipients of funding. For seven of those PIs, collaborations have proved sufficiently fruitful that funding has been awarded for a second year.

The positive impact of UCDRD funding is manifested not only in the cutting-edge research it has enabled but also in the lasting legacy of an extensive list of new experimental capabilities developed at the NHMFL. Collaborations funded in FY 1998 include

- Neutral Fermions at Filling Factor 1/2 (UC Berkeley)
- Magnetotransport in Non-Fermi-Liquid Systems (UC San Diego),
- High-Field Transport and Magnetization in Magnetic Materials (UC Irvine),
- Magnetotransport and Photoluminescence Spectroscopy in Two-Dimensional Electron System (UC Los Angeles),
- Photoluminescence in Polymers (UC Santa Barbara), and
- Heat Capacity in High-Temperature Superconductors (UC Berkeley).

Future collaborations to be funded include

- Photoluminescence and Absorption Spectroscopy in Semiconductors (UC Santa Barbara),
- Magnetotransport and Heat Capacity of Correlated Electron Systems (UC Riverside),
- Nuclear Magnetic Resonance in High Magnetic Fields (UC Los Angeles),
- Magnetotransport of High-Temperature Superconductors (UC Berkeley), and
- Dynamics of Random Magnetic Systems (UC Riverside).

Typically, UCDRD funding has covered travel expenses, laboratory consumables (such as cryogens), and small equipment grants, which are necessary to seed the research

collaboration between the UC PI and the NHMFL. In addition to continuing the commitment to these small proposals, the NHMFL is developing a second funding philosophy designed to expand the leverage of the UCDRD grant to forge strong UC–Los Alamos collaborations. In order to cement longer-term collaborations with the UC PIs, proposals are encouraged that include support at a level sufficient to allow graduate students and/or postdoctoral researchers to perform a substantial fraction of their total research program at the NHMFL. Two examples of this are the recently approved collaboration with UC Riverside (Dynamics of Random Magnetic Systems) and the proposal under development with UC Santa Barbara (Photoluminescence and Absorption Spectroscopy in Semiconductors). The NHMFL continues to be pleased with the dramatic effect that the UCDRD grant has on its research portfolio and on its continuing development of pulsed-magnetic-field research.

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Research and Education Utilizing the NHMFL: Physics of Quantum Hall Devices in Ultra-High Magnetic Fields

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Abstract

In recent years, magnetoluminescence spectroscopy has been used widely to study the two-dimensional electrons of semiconductor quantum structures in the quantum Hall-effect regime. Thanks to the newly commissioned 60-T long-pulse magnet at Los Alamos National Laboratory, we are now able to obtain over 1000 photoluminescence spectra during a single magnetic field pulse, providing a "video" of the spectral evolution in response to the magnetic field (Fig. 1). The power of this new magnet also provides us with opportunities to explore physics in a new regime of parameters. By using this magnet, we have been able to follow our last year's effort with the short-pulse magnet and to find definitive evidence of a new excitonic state in the

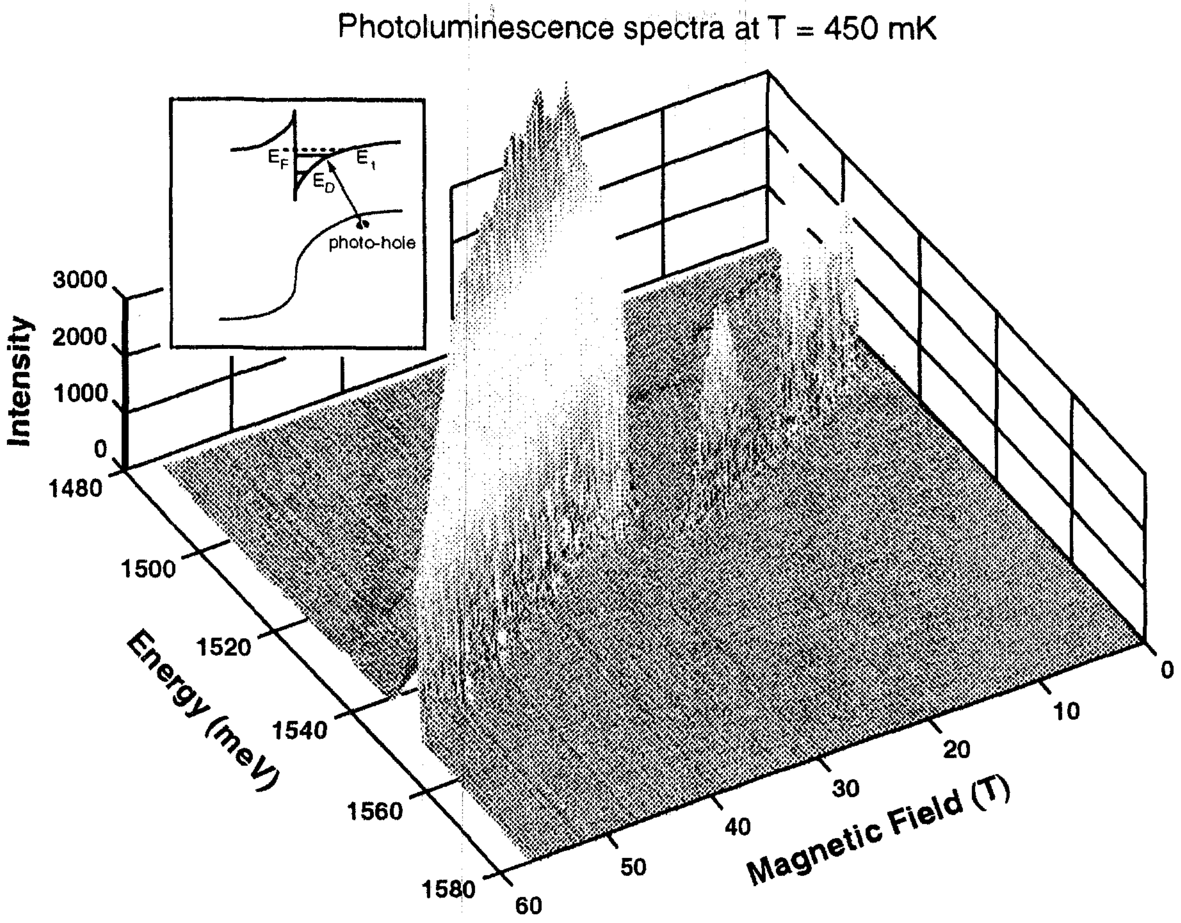

Fig. 1. Photoluminescence spectra of the two-dimensional electron gas in a three-dimensional plot. Data were taken with the new 60-T pulsed magnet, and 1500 spectra were collected in 1.5 seconds. The inset is a schematic band diagram of the semiconductor heterostructure used for the study.

anomalous photoluminescence spectrum observed at high magnetic fields.

In a high-density GaAs/AlGaAs heterostructure, because of the proximity of the Fermi level to one of its quantum subbands, little energy is required for the equilibrium two-dimensional system to interact strongly with the photoexcited, nonequilibrium electrons and holes. Thus, electrons can be rearranged near the photoexcited holes to form a many-body excitonic state (a Mahan exciton). Our data show a good correlation with the calculated dependence of the Fermi energy on the magnetic field; however, the most striking feature in the data is the unexpected emission line that appears suddenly at a critical field near 30 T. This magnetic field corresponds to a filling factor of 2 for the equilibrium two-dimensional electron system, and the new emission line exhibits a giant red-shift in energy (>10 meV). It is believed that the new line is a spin-polarized exciton state that results once the photoexcited holes undergo a phase transition from a free state to a spatially localized bound state (much like the Mott transition). This transition is a consequence of the competition between the built-in repulsive potential of the heterostructure and the attractive potential of the electrons that can occur in high magnetic fields due to the strong reduction of the screening strength in the quantum limit.

In another photoluminescence experiment, we have probed the two-dimensional holes in a p-type GaAs/AlGaAs heterostructure. The two-dimensional hole system is particularly interesting because of the large ratio of the correlation energy to the kinetic energy. At high magnetic fields, we found that the spectra was dominated by a new high-energy line and another low-energy line (at energy even lower than the conventional lines for two-dimensional hole systems). These new observations are believed to be associated with the highly correlated Hall insulator phase.

In another experiment, by using the 30-T DC magnet at the National High Magnetic Field Laboratory, we have studied transport properties of GaN semiconductor hetero-structures, the same material for making blue lasers. We found large anisotropy in the quantum transport of the two-dimensional electron gas at the AlGaAs/GaN interface. This anisotropy is due to the unique band structure of the material.

Our experiments provide us insights into the quan-tum interactions that govern the electrical and optical properties of the low-dimensional systems. These results can also have an impact on the realization of new devices whose fabrication and operation are based on semiconductor structures of similar type.

Refereed Publications

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Lee, X.Y., H.W. Jiang, Y. Kim, and W.J. Schaff, "Observation of a Discontinuous Red-Shift in the Emission Spectrum of a Two-Dimensional Electron Gas" (to be published in *Phys. Rev. B*).

Wong, L.W., S.J. Cai, R. Li, K.L. Wang, and H.W. Jiang, "Magnetotransport Study on the Two-Dimensional Electron as in AlGaN/GaN Heterostructure," *Appl. Phys. Lett.* 73, 1391 (1998).

Nonrefereed Publications

Lee, X.Y., H.W. Jiang, Y M. Kim, and W. Schaff, "Discontinuous Red-Shift in the Emission Spectrum of a Two-Dimensional Electron Gas," in *National High Magnetic Field Laboratory 1998 Annual Report,* Kathy Hedic and Jeff Simon, Eds. (Florida State University, Tallahassee, 1998), Vol. 1.

Lee, X.Y., S. Dultz, and H.W. Jiang, Y.M. Kim, and W. Schaff, "Spin-Resolved Photolumi-nescence Probe of Two-Dimensional Holes in a p-Type GaAs/AlGaAs Heterostructure," in *National High Magnetic Field Laboratory 1998 Annual Report,* Kathy Hedic and Jeff Simon, Eds. (Florida State University, Tallahassee, 1998), Vol. 1.

Presentations

Lee, X.Y., H.W. Jiang, Y.M. Kim, and W. Schaff, "Observation of Anomalous Photoluminescence Spectrum in High Magnetic Fields: Evidence of a New Excitonic State," National Science Foundation NHMFL Site Visit, Tallahassee, FL, 1998 (contributed).

Lee, X.Y., H.W. Jiang, Y.M. Kim, and W. Schaff, "Studies of High-Field Fermi-Edge-Induced Magnetoluminesence in Pulsed Magnets," Meeting of the American Physical Society, Los Angeles, CA, March 16–20, 1998 (contributed).

Wong, L.W., S.J. Cai, R. Li, K.L. Wang, and H.W. Jiang, "High-Field Magneto-transport Study on the Two-Dimensional Electron as in AlGaN/GaN Hetero-structure," Meeting of the American Physical Society, Los Angeles, CA, March 16–20, 1998 (contributed).

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Research and Education Utilizing the NHMFL: Neutral Fermions at Filling Factor 1/2

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Abstract

Particle-hole symmetry poses a road block to our understanding of the physics of a two-dimensional electron gas at filling factor 1/2. An amazing fact about half filling is that aside from a large Hall conductance, the behavior of electrons near nu=1/2 resembles that near a zero field.

In conventional wisdom such behavior is explained in terms of the "composite Fermi liquid theory." In this theory one views each electron as a composite fermion carrying two quanta of fictitious magnetic flux. The idea is that at filling factor 1/2, the fictitious flux cancels the real flux on average. As a result, the composite fermions move in a zero net magnetic field. The last statement offers an explanation of the origin of the zero-field behavior seen experimentally. This theory has stimulated a large body of work.

A few years ago we realized that the notion of composite fermions moving in a zero net magnetic field is at odds with the particle-hole symmetry in the lowest Landau level. Such symmetry constrains the composite fermion Hall conductance to be $-e^2/2h$, a behavior not expected for particles moving in a zero magnetic field. This realization casts the origin of the zero-field behavior into shadow again.

In two papers, we proposed an alternative explanation of the experimental result. In a nutshell, the idea is that the quasi particles at half filling are fermionic dipoles. The composite fermion is a member of the dipole. While the dipole motion is zero-field-like because of its charge neutrality, the intradipole motion of composite fermions is strongly Hall-like.

The half-filled Landau level problem is the most notable unsolved problem in the quantum Hall effect. We believe that the dipole picture satisfactorily answered all the qualitative issues concerning this problem.

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Lee, D.-H., "An Unsettled Issue in the Theory of the Half-Filled Landau Level" (submitted to *Phys. Rev. B*).

Lee, D.-H., and X-G Wen, "Edge Tunneling in Fractional Quantum Hall Regime" (submitted to *Phys. Rev. Lett.*).

Award

D.-H. Lee, Fellow, American Physical Society, 1998.

Contents

Abstracts

00	9858	BooNE Collaboration *William C. Louis, Los Alamos; Gordon J. VanDalen, UC Riverside*
00	9859	Satellite Imaging Spectrometry *Sigfried Gerstl, Los Alamos; Dar A. Roberts, UC Santa Barbara*

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Ultrafast Holographic Materials

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Eric Maniloff, LANL

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Abstract

Charge-transfer nonlinear optical polymers represent a tremendous opportunity; these materials offer the promise of truly unique properties—properties which mimic the performance of photorefractive materials but on ultrafast (picosecond) time scales. Such materials will allow investigation into ultrafast optical switching (beam steering) and information-processing applications, that is, ultrafast photonic applications that are impossible today with any known materials. The goal of the research program is to develop the next generation of charge-transfer nonlinear optical polymers with high temporal-diffraction efficiency, that is, materials with diffraction efficiencies near unity and with picosecond response times. Ultrafast materials with such high diffraction efficiencies for a single picosecond pulse will make possible image processing with inexpensive, low-power pulsed solid-state lasers, which will be widely available commercially in the near future.

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McBranch, D., "Supramolecular Photoinduced Charge Transfer Materials for Nonlinear Optics," *Curr. Opin. Solid State Mater. Sci.* **3**, 203 (1998).

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Vacar, D., A. Dogariu, and A.J. Heeger, "Ultrafast Gain and Excited State Absorption in Luminescent Polymers: Pump Wavelength Invariance," *Chem. Phys. Lett.* **290**, 58 (1998).

Presentations

Kraabel, B., "Ultrafast Spectroscopic Holography in Conjugated Polymers," International Conference on the Science and Technology of Synthetic Metals, Montpellier, France, July 1998 (contributed).

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Patent

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9838

Integrating Los Alamos National Laboratory's Transportation Analysis Simulation System (TRANSIMS) and UC Riverside's Comprehensive Modal Emissions Model

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Abstract

It has become apparent in the past few years that significant improvements are needed in our ability to characterize emissions from vehicles traveling on our roadways. Numerous studies have shown that under most on-road operating conditions, actual vehicle emissions can

differ dramatically from what is predicted by current transportation and mobile-source emissions models. The primary problem lies in the fact that both transportation models and emissions models used to date lack the level of detail required to produce accurate emissions inventories. As a result, two major programs have been initiated by the U.S. government to develop both a better transportation simulation model and a better set of emissions models.

In one program, Los Alamos researchers are currently developing a high-level-of-detail traffic simulation model that can be applied to large regional networks. This research is sponsored by the Federal Highway Administration and is known as the Transportation Analysis Simulation System (TRANSIMS) project. When complete, the TRANSIMS model will be used for traffic flow analysis, traffic planning, transportation control measure evaluation, and air-quality impacts. In a second program, researchers at UC Riverside College of Engineering, Center for Environmental Research and Technology, are currently developing a comprehensive modal emissions (CME) model that predicts emissions output as a function of vehicle operating mode (e.g., idle, cruise, various levels of acceleration/deceleration). In this program, highly time-resolved emissions and vehicle operation data are being collected through state-of-the-art dynamometer testing for a wide range of vehicle technology types (more than 300 vehicles). These data are then being used to establish and calibrate a set of analytical functions that describe the physical phenomena associated with vehicle operation and emissions production.

The primary objective of this UC Directed Research and Development project is to integrate the Los Alamos TRANSIMS model and the UC Riverside CME model in order to establish a powerful tool that can produce accurate emissions inventories. In the first year of research, both teams generated a detailed list of interfacing issues and created a preliminary methodology for integrating the two models. In the second year of research, this methodology has been refined, using unique approaches to integrate TRANSIMS coarse-stepped velocity profiles with the required CME input. As the two models are successfully integrated in the third year, it will be possible to use the models together to produce accurate emissions inventories for both "microscale" (e.g., intersections, highway links) and "macroscale" (i.e., regional level) traffic scenarios. The resulting modeling tool will be of immense importance, particularly in light of the conformity requirements of the Clean Air Act Amendments of 1990 and the aggressive implementation of transportation control measures, intelligent transportation systems, alternative-fuel vehicles, and more sophisticated inspection and maintenance programs contained in most state air-quality management plans.

Refereed Publications

Barth, M., G. Scora, and T. Younglove. "Estimating Emissions and Fuel Consumption for Different Levels of Freeway Congestion" (submitted to *Transp. Res. Rec.*).

Williams, M., G. Thayer, and L. Smith. "A Comparison of Emissions Estimated in the TRANSIMS Approach with Those Estimated from Continuous Speeds and Accelerations" (submitted to *Transp. Res. Rec.*).

Nonrefereed Publications

Barth, M., M. Ross, F. An, G. Scora, C. Levine, and T. Wenzel. "NCHRP Project 25-11: The Development of a Comprehensive Modal Emissions Model" (submitted to *Nat. Coop. Highw. Res. Program Rep.*).

Presentations

Barth, M., G. Scora, and T. Younglove. "Estimating Emissions and Fuel Consumption for Different Levels of Freeway Congestion," 78th Annual Meeting of the Transportation Research Board, Washington, DC, January 1999 (contributed).

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Institutional and Technical Issues Regarding Nuclear Stewardship: Radioactive Waste and Nuclear Materials Management

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Graduate Students: Luca Gratton and David Hutchinson, Department of Nuclear Engineering, UC Berkeley; Andrew Koehler, Goldman School of Public Policy,

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Abstract

Our objective is to develop a new, integrated, and comprehensive understanding of the challenges involved in designing and carrying out long-term management strategies for nuclear materials and other technologies with intrinsic complexity and hazard.

In part, this work applies analytic approaches from the social sciences and policy analysis to identify requirements and design criteria for management systems that simultaneously consider technical and social-institutional constraints having to do with organizational dynamics, safety, regulation, and public participation in decision processes. This technique enables designers of such technical systems to take into account a larger array of factors, including those they have encountered in the past as extrinsic challenges (such as intrusive regulation or public opposition) but have been unable to incorporate into their own work context in a meaningful and practical way. Thus, rather than having to take a reactive stance in a situation fraught with technical and political uncertainties, scientists and policymakers can anticipate and address social and institutional challenges.

One project task has been to examine the public and expert discourse about plutonium disposition, explaining conflicting accounts and assessments through their particular logical and interpretational contexts. This "discourse analysis," adopted from the disciplines of rhetoric and linguistic analysis, helps clarify disagreements and points to agreement where it exists and provides a basis for various participants in dialogues on controversial technical issues to understand each other. Drawing on published material and more importantly on interviews with scientists at Los Alamos and Lawrence Livermore National Laboratories, as well as other participants in the debate (from policy advisors to local activists), researchers mapped the various perspectives on plutonium immobilization and MOX fuel as disposition strategies. Researchers also initiated an examination of the controversy over the DOE program to ship spent fuel from foreign research reactors through the Concord Naval Weapons Station to the INEEL. This program met with local opposition and a lawsuit despite support from Greenpeace and the Natural Resources Defense Council. This work continues and is being prepared for submission for publication.

Researchers examined a number of waste-minimizing and proliferation-resistant nuclear-reactor concepts and fuel cycles for deployment domestically and internationally. The estimated lifetime of variants of the long-life reactor core is approximately 20 years on a single core load, an order of magnitude more than the time between refueling of current commercial nuclear power reactors. Reactors with these long-life cores may operate for years in a remote location without refueling, operated by lightly trained personnel. This concept separates technical activities that are normally closely associated with nuclear energy production in time and space in a provocative and interesting way.

The research group has begun to integrate models for technical performance and safety with socio-institutional studies to understand what constitutes acceptable repository performance, including attendant public health risks arising from the geologic disposal of nuclear wastes. Researchers are extending the existing conceptual framework from examination of plutonium disposition to other waste forms. We ultimately hope to provide a framework in which technical design receives guidance from the disparate performance measures of expected project cost, anticipated public health

risk and expected public perception. The use of decision-theoretic models such as game theory, multi-attribute utility analysis, and directed flow graphs are being explored. Also, further results of our study on underground criticality were published during this funding period.

Over the past year, project researchers have engaged in work with laboratory scientists in various ways, including intensive on-site observation and analysis, cooperative efforts in systems modeling and project evaluation, as well as interviews and discussions. Collaborations and interactions on a range of projects and issues have led to proposals for related future projects.

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La Porte, T.R., "Institutional Strain and Precarious Values in Meeting Future Nuclear Challenges: External Elements," Los Alamos National Laboratory's Community Outreach Council, Los Alamos, NM, December 1997 (invited).

Peterson, P.F., "Relative Proliferation Attractiveness of Reprocessing Waste and Spent Fuel: Implications for Long-Term Safeguards Technical Requirements," International Symposium on Energy Future in Asia/Pacific Region, Honolulu, HI, March 27–28, 1998 (invited).

9840
Research with SuperKamiokande

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Abstract

Neutrinos have been observed from only three different astrophysical sources: the sun, the atmosphere, and a supernova. We know that there are far fewer neutrinos produced from the sun than we expect, and the flavor composition of the neutrinos produced by cosmic-ray interactions in the earth's atmosphere is very different than expected. For the first time, data from SuperKamiokande (SuperK) has convincingly shown evidence for neutrino oscillations using the beam of atmospheric neutrinos. This is about a dozen years since the first suggestion of an "atmospheric neutrino problem" in data from the Irvine-Michigan-Brookhaven experiment (in Haines et al., *Physical Review Letters* 41, 1986). The oscillation parameters appear to suggest that muon-neutrinos are fully mixed with tau-neutrinos, and their mass-squared difference is in the range of 10**$^{-2}$ to 10**$^{-3}$ eV**^{2}. This evidence, along with the lack of neutrinos from the sun and the so-called liquid scintillator neutron detector anomaly, has provided many puzzles for both theorists and experimentalists to unravel.

Calibration of the detector has been accomplished using a radioactive source and fission counter, developed with colleagues at Los Alamos. New sources have been identified and, if desired by the collaboration, will be provided. These developments may also be useful in other applications.

New image analysis methods have been developed for use in studying data from the Milagro gamma-ray observatory. When these methods are complete, they will be studied to determine their usefulness for the study of SuperK data.

Atmospheric neutrinos are now known to oscillate between different flavor states. A natural next question is, as in the kaon system, whether charge-parity (or charge-parity-time) violation occurs in these oscillations. During the next year, the ability of SuperK to address this question will be examined in detail. If it appears fruitful, examination of the consequences to the experiment, including changes that might be made, will be undertaken.

Refereed Publications

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Fukuda, Y., et al., "Measurements of Radon Concentration at SuperKamiokande" (to be published in *Phys. Lett. B*).

Fukuda, Y., et al., "Measurement of a Small Atmospheric $\nu_{\mu}/\nu_{\varepsilon}$ Ratio," *Phys. Lett. B* 433, 9 (1998).

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Haines, T., "The Case of the Missing Cosmic Neutrinos," Colloquium at the Enrico Fermi Institute, University of Chicago, Chicago, IL, November 1998.

Haines, T., "Latest SuperKamiokande Results," Seminar on Nuclear and Particle Physics, Los Alamos National Laboratory, Los Alamos, NM, December 1997.

9841

Independent Risk and System Safety Analysis

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Graduate Students: Richard Moushegian: Department of Political Science, UC Los Angeles; Jorge R. Palamara, Department of Economics, UC Los Angeles

Abstract

There were three principal tasks for this project. The first task was to help develop a charter for the UC Center for Risk Analysis and System Safety, which was established in August 1998. Its focus is developing research in risk analysis. A charter was developed, and the UC Office of the President provided funding for three years to cover administrative costs. This work is an integral part of the center.

The second task was to develop alternative approaches to a safety philosophy for US Department of Energy operations on nuclear weapons. Currently, the operations are analyzed to determine their associated

hazards, and engineered or administrative controls are identified to mitigate either their occurrence or their consequences. A safety philosophy would help in establishing criteria by which we could determine when these controls and the associated lower risks were acceptable.

Any proposed safety philosophy must take into account the fundamentally different nature of risks posed by the assembly and disassembly of nuclear weapons compared with other risks. For this work, "other risks" are categorized as technological (e.g., nuclear power and chemical plants) or natural (e.g., earthquakes and tornadoes). The different aspects of risk and their relationship to safety philosophy are examined in this work.

The effort this year was devoted to understanding natural and nuclear technological risks. The objective was to determine what their role, if any, should be in the development of plausible bases for potential approaches to safety philosophy. The Pantex nuclear weapons facility, which is located in the vicinity of Amarillo, Texas, was chosen for study.

The work began with a reasonably broad review of prior publications in the field, along with an examination of published positions by governmental bodies in the United States and a detailed review of Pantex safety documents, including the Hazard Analysis Report Handbook and the Authorization Basis for Control Document. In particular, the safety philosophy adopted by the U.S. Nuclear Regulatory Commission (NRC) for commercial nuclear power plants and the risk management approach adopted by the Netherlands were found to be useful. The U.S. Environmental Protection Agency (EPA) approach is not as relevant because the EPA is dealing with chronic exposures rather than accidents.

Comparative risks play a large role in the bases used by the NRC and by the Netherlands for establishing risk policy, and comparative risks are used heavily in this research effort. To supplement the statistical information available for the nation on accident risks and on all causes of mortality, it was decided to analyze some specific, less common accident risks for the city of Amarillo. Individual and societal risks at Amarillo were estimated for severe earthquakes, very powerful tornadoes, and large in-city, railroad car crashes involving very hazardous materials. An outline of the report and most of its draft sections had been prepared by the end of the research year.

The third task was to work with Los Alamos to develop a plan for addressing weapon safety themes. The research participants met and established a background and basis for future work on safety theme development.

9842
Integrated Catalysis Program

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Postdoctoral Fellows: Neil J. Henson, Cybele Hijar, and Susan Crawford, LANL

Graduate Students: Ghansham Panjabi and Brian Enderle, UC Davis; Brian Adair and Randall Hatfield, UC Santa Barbara

Abstract

During the past year, we have continued to focus on the synthesis, structure, and reactivity of metal ions and metal clusters in microporous materials. We have continued our work on probing the structure of microporous materials using solid-state nuclear magnetic resonance (NMR) techniques. We have used ^{129}Xe solid-state NMR spectroscopy to define mobility and binding of xenon over a very wide range of temperatures but at very low loading of xenon (1 xenon/alpha cage). Our results have indicated that intercrystalline diffusion is much slower than intracrystalline diffusion and that xenon atoms spend much of the time in the alpha cages of zeolite Y.

In other similar studies, metal carbonyl clusters and naked metal clusters have been placed into the supercage of zeolite Y. Again, study of ^{129}Xe NMR spectroscopy over a wide temperature range and at very low loading of xenon have indicated the surprising result that xenon is less strongly bound on metal clusters such as Ir_4, Ir_6, and Rh_6 than on the zeolite walls. However, there is a large change in xenon chemical shift in the presence of $Ir_4(CO)_{12}$ clusters, indicating that xenon interacts somewhat more strongly than the zeolite walls. Negligible shifts are observed for the larger $Ir_6(CO)_{16}$ and $Rh_6(CO)_{16}$ clusters, perhaps because the increased size of the cluster excludes xenon entirely from the cage, thus eliminating any xenon-cluster interactions. These data lead to a different interpretation of xenon-cluster interactions than that proposed in the literature from room-temperature xenon NMR studies.

In other work, we have investigated structural aspects of metal-substituted microporous materials, using the influence of paramagnetic metal ions. The influence

of the paramagnets on the NMR properties of framework constituents allow us to determine whether the paramagnetic ion is located within the framework structure or is simply ion-exchanged onto the surface of the pore. Along these lines, we have also investigated the chemistry and structures of titanium and cobalt ions held within the framework structures of silicates and aluminophosphates by using theoretical methods. We benchmarked the Co-$AlPO_4$ studies against well-known molecular Schiff's base complexes and studied the oxygen chemistry of both the Co-$AlPO_4$ and Co-Schiff's base complexes. We found that the tetrahedral cobalt ions in the AlPO has no tendency to bind O_2. This result has implications for the mechanism of Co-$AlPO_4$ mediated oxidation of hydrocarbons.

Other research involving the entrapment of catalytically active, small titanium silicate clusters within the mesoporous network of MCM-41 is directed at obtaining catalysts that have the activity and selectivity of homogeneous catalysts with the advantages of a solid, heterogeneous catalyst. Our research on one interesting titanium silicate cluster system has shown that these molecular clusters are not held tightly within the pores and that they leach from the pores under catalytic conditions, contrary to what has been reported in the literature. Our subsequent work has been directed at the synthesis of modified titanium silicate clusters that can be anchored onto surfaces, thus rendering them stable to leaching during reaction.

An additional area that we have been investigating is the attempted preparation of novel microporous framework compounds that may be useful as catalysts. Our strategy has been to investigate tin phosphate and phosphonate chemistry in the hopes of discovering new and novel framework structures. A number of new phosphonate compounds have resulted, some of which have a number of unusual structural motifs.

Refereed Publications

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Henson, N.J., P.J. Hay, and A. Redondo, "Density Functional Theory Studies of the Binding of Molecular Oxygen with Schiff's Base Complexes of Cobalt," *Inorg. Chem.* **38**, 1618 (1999).

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Labouriau, A., T. Pietrass, W.A. Weber, B.C. Gates, and W.L. Earl, "Temperature Dependence of NMR Chemical Shifts of ^{129}Xe in the Alpha-Cages of NaY Zeolite" (to be published in *J. Phys. Chem.*).

Labouriau, A., G. Panjabi, B. Enderle, T. Pietrass, B.C. Gates, W.L. Earl, and K.C. Ott, "^{129}Xe NMR Spectroscopy of Metal Carbonyl Clusters and Metal Clusters in Zeolite NaY" (to be published in *J. Am. Chem. Soc.*).

Labouriau, A., T. Pietrass, S.N. Crawford, W.A. Weber, G. Panjabi, B.C. Gates, and W.L. Earl, "Probing Zeolite Internal Structures Using Very Low Tempeature ^{129}Xe NMR," *Proceedings of the 12th International Zeolite Conference*, M.M. Treacy et al., Eds. (Materials Research Society, Warrendale, PA, 1999), Vol. IV, p. 2265.

Ott, K.C., J. Rau, and F.M. de Rege, "Stability and Deactivation of Titanium Silicate Catalysts," *Abstr. Pap. Am. Chem. Soc.* 217 (1), 187 COLL (1999).

9846

Influenza Data Analysis

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Abstract (1)

The hemagglutinin (HA) gene of influenza viruses encodes the major surface antigen against which neutralizing antibodies are produced during infection or vaccination. We examined temporal variation in the HA1 domain of HA genes of human influenza A (H3N2) viruses in order to identify positively selected codons. Positive selection is defined for our purposes as a significant excess of nonsilent over silent nucleotide substitutions. If past mutations at positively selected codons conferred a selective advantage to the virus, then additional changes at these positions may predict which emerging strains will predominate and cause epidemics.

We reported previously that a 38% excess of mutations occurred on the tip or terminal branches of the phylogenetic tree of 254 HA genes of influenza A (H3N2)

viruses. Possible explanations for this excess include processes other than viral evolution during replication in human hosts. Of particular concern are mutations that occur during adaptation of viruses to grow in embryonated chicken eggs in the laboratory. Because the present study includes 357 HA sequences (a 40% increase), we were able to analyze separately those mutations assigned to internal branches. This allowed us to determine if mutations on terminal and internal branches exhibit different patterns of selection at the level of individual codons. Additional improvements over our previous analysis include correction for a skew in the distribution of amino acid replacements across codons and analysis of a population of phylogenetic trees rather than a single tree. The latter improvement allowed us to ascertain whether minor variation in tree structure had a significant effect on our estimate of the codons under positive selection.

Using the larger data set and the modified methods, we confirmed a large (40%) excess of changes on the terminal branches. We also found an excess of changes on branches leading to egg-grown isolates. Furthermore, when we used only mutations assigned to internal branches, nine of the 18 amino acid codons identified to be under positive selection to change were not under positive selection on the terminal branches. Thus, although there is overlap between the selected codons on terminal and internal branches, the codons under positive selection on the terminal branches appear to differ somewhat from those of the internal set. We also observed that there is an excess of positively selected codons associated with the receptor binding site and with the antibody combining sites. This association may explain why the positively selected codons are restricted in their distribution along the sequence. Our results suggest that future studies of positive selection should focus on changes assigned to the internal branches, as certain of these changes may have predictive value for identifying future successful epidemic variants.

Abstract (2)

Sequences were annotated to give details on sources of recombinants, mutational variants, antigenic type, and other relevant information that is not contained in the original GenBank record. This "value added" is a feature of specialized databases, such as the Influenza Sequence Database. We also compiled a table of epidemic (i.e., dominant) strains of each of the three cocirculating types of influenza virus. By researching publications of the Centers for Disease Control and the World Health Organization, we have ascertained the strains that were primary causes of excess mortality resulting from influenza in each of the past ten years. This information provides the basis for reference sets that will be placed on the public Web site, together with the matching sequence information, for user analysis.

Sequence variation in the antigenic and receptor binding sites of human hemagglutinin HA is of both functional and epidemiologic interest in understanding trends in the evolution of human influenza type A. Using two approaches, we analyzed the amino acid sequence changes that occurred in the antigenic drift of hemagglutinin HA during the years 1968–1996.

The first approach is entirely sequence-based and quantifies, using the concept of mutual information taken from information theory, the degree of covariation (nonindependence) between mutations occurring in different sequence positions. We found that certain pairs of sites, which are often well separated in physical space within the folded protein, do not mutate independently but instead display considerable and statistically significant covarying mutations.

The second approach incorporates both sequence and structural information. Using the Hong Kong 1968 hemagglutinin structure and wild-type

sequence to define environments, we calculated Eisenberg 3D-1D scores for sequences taken from the antigenic drift period 1968–1996. These profile scores measure the compatibility of each residue with its physico-chemical environment as defined by the hemagglutinin structure. A standard correlation analysis was performed on the profile scores.

We find that certain pairs of sites display considerable, statistically significant correlations in their 3D-1D scores and that this correlation illuminates the physical significance of the mutual information scores. Furthermore, variable sites separate into two classes of sites according to the 3D-1D scores: sites with a poor score for all amino acid replacements and sites with a good score for all amino acid replacements. Under investigation is the relation of sites with poor scores, that is, those positions that predominantly use amino acids that are incompatible with the local physical environment, to the sites identified by our UC Irvine collaborators as undergoing positive selection. This work has been written as a preprint and is being finalized for submission for publication.

In a separate investigation, we have analyzed the same set of drift sequences by compressing the information in each sequence into a space of ten dimensions. The first significant result of this investigation is that ten dimensions are sufficient to preserve the second-order statistics of the sequences to a high degree of accuracy. Hence, the covarying mutations described above can be represented by a rather small space of interactions. Investigation is continuing of the relation of this ten-dimensional representation of sequences to more conventional representations of sequence relationships by means of a classic phylogenetic tree. This work is in progress and so far is not published.

We propose to continue our investigation of sites with varying mutations in the hemagglutinin protein of influenza. Using the 1968 Hong Kong hemagglutinin x-ray crystal structure and the associated wild-type sequence allowed us to define Eisenberg environmental classes for each position in the sequence. We found that certain variable positions consistently substitute amino acids that are incompatible with the local physico-chemical environment. We propose to investigate whether immune pressure may be causing this use of incompatible residues in these positions and how these positions relate to those positions determined by our UC Irvine collaborators to be undergoing positive selection.

In additional proposed work designed to test the statistical significance of any quantity computed from a set of sequences related by a phylogenetic tree, we plan to implement a "null-model" approach, in which sequence will be evolved down the phylogenetic tree, assuming that mutations in each position occur independently.

Finally, we propose to continue our investigation of compressing the information in variable positions of the hemagglutinin protein into a low dimensional space. Issues that will be investigated include (a) the relation of the distances of sequences based on the representation in the low dimensional space to "evolutionary distance" based on comparing mutations in individual sequence positions and (b) the minimial network of interactions among positions that will reproduce the observed first- and second-order statistics, that is, the observed variation, and covariation.

Refereed Publication

Bush, R.M., W.M. Fitch, C.A. Bender, and N.J. Cox, "Positive Selection on the H3 Hemagglutinin Gene of Human Influenza Virus A" (submitted to *Mol. Biol. Evol.*).

Presentations

Bush, R.M., "Predicting the Evolution of Human Influenza A," Theoretical Biology and Biophysics Group, Los Alamos National Laboratory, Los Alamos, NM. January 21–22, 1998 (invited).

Bush, R.M., "Predicting the Evolution of Human Influenza A," Gordon Conference on Molecular Evolution, Ventura, CA, January 25–30, 1998 (contributed).

Bush, R.M., "Predicting the Evolution of Human Influenza A," University of California, Irvine, CA, October 30, 1998 (invited).

Fitch, W.M., "Getting the Flu before It Gets You," Cambridge University Alumni Association, UK, September 26, 1988 (invited).

Fitch, W.M., "Getting the Flu before It Gets You," UC Irvine Distinguished Faculty Lectureship, October 8, 1988 (invited).

Fitch, W.M., "Getting the Flu before It Gets You," American Academy of Arts and Sciences, Chicago, IL, October 10, 1988 (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," Biology Department, University of California, Los Angeles, CA, February 18, 1998, (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," University of Texas, Houston, TX, April 7, 1998 (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," Centers for Disease Control, Atlanta, GA, May 15, 1998 (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," University of Greifswald, Greifswald, Germany, June 25, 1998 (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," University of Bielefeld, Bielefeld, Germany, June 29, 1998 (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," Hennig Society, Sao Paolo, Brazil, September 24, 1998 (invited).

Fitch, W.M., "Predicting Human Influenza Evolution," Evolution Group, University of California, Los Angeles, CA, October 10, 1997 (invited).

9847
Integrated Structural Biology of Protein-Nucleic Acid Complexes

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Abstract

Cellular repair of DNA double-strand breaks (DSBs) is required for normal development of the immune system and normal resistance to ionizing radiation. The repair of DSBs in eukaryotic cells can proceed by two pathways: nonhomologous end-joining (NHEJ) and homologous recombination. In mammalian cells, it is clear that nonhomologous repair of DSBs is highly active and plays a major role in radiation resistance and immune system development. In this end-joining pathway, the free ends of broken DNA molecules are joined together without reference to an undamaged version of the chromosome. Unlike homologous recombination, NHEJ may result in the introduction of mutation. Nonetheless, NHEJ provides a critical means of repairing otherwise lethal DNA damage.

Several proteins required for DSB repair have been identified by the characterization radiation-sensitive rodent cell lines shown to be deficient in the rejoining of radiation-induced DSBs. The deficiencies in some cell lines were found to be the result of deficiencies in the activity of the DNA-dependent protein kinase (DNA-PK). The DNA-PK holoenzyme consists of three protein subunits. In vitro, the assembly of purified DNA-PK on DNA ends is well characterized. The DNA-binding subunit, known as Ku, is a stable heterodimer of 70 and 86 kD subunits which binds to free DNA ends in a sequence-independent manner. When bound to DNA, the Ku70/80 complex can stabilize the association of the 460 kD DNA-PK catalytic subunit (DNA-PKcs) thus forming the DNA-PK holoenzyme. On the basis of these properties, it has been proposed that DNA-PK functions in DNA repair by phosphorylating protein substrates that colocalize with it on the ends of broken DNA.

To gain insight to the structure-function relationships critical to the cellular repair of DSBs, we have determined the structure of the DNA-PKcs using three-dimensional image reconstruction from cryoelectron micrographs. We have collected over 1600 cryoelectron micrographs of the DNA-PKcs purified from HeLa cell nuclear extracts (Fig. 1). Over 9000 individual particle images were processed to yield a three-dimensional reconstruction at 21-Å resolution. The reconstruction of the DNA-PKcs subunit is the first reported structure of a member of this family of protein kinases. The reconstruction shows that DNA-PKcs has an open, pseudo two-fold symmetric structure with a gap separating a crown-shaped top from

a rounded base (Fig. 2). The pseudo two-fold symmetry may allow the insertion of two DNA ends from the two opposing faces of the catalytic subunit or association with two regulatory Ku heterodimers simultaneously. Numerous cavities and tunnels are observed throughout the DNA-PKcs structure, suggesting that the interaction between DNA-PKcs and DNA may involve the internalization of double-stranded DNA ends. Our publication of the DNA-PKcs structure has provided the first indication that the DNA-PKcs may have adequate internal volume to accommodate the simultaneous interaction with two DNA ends. These data suggest a model in which the repair of DNA DSBs is facilitated by the stabilization of the broken DNA strands by interactions with the DNA-PKcs. This model is further supported by the observation that the DNA binding subunit of the DNA-PK enzyme is capable of physically holding DNA ends together and thus enhancing the activity of eukaryotic DNA ligases. Other proteins with homology to DNA-PKcs include the protein defective in humans suffering from ataxia-telangiectasia (ATM) and proteins implicated in cell cycle regulation and in aging. Taken together with our recent observation (published) that the ATM protein binds to and is activated by DNA ends, these data further suggest that this family of protein kinases may share similar modes of DNA interaction and catalytic activation.

Ultimately, we must understand how the DNA-PK holoenzyme, composed of DNA-PKcs and the DNA binding component known as Ku, assembles on the ends of DNA, how this assembly results in kinase activation, and how damaged DNA ends are spatially oriented for repair within the DNA-PK complex. Work is currently underway to build a high-resolution model of DNA-PK in association with DNA and Ku. This model will be used

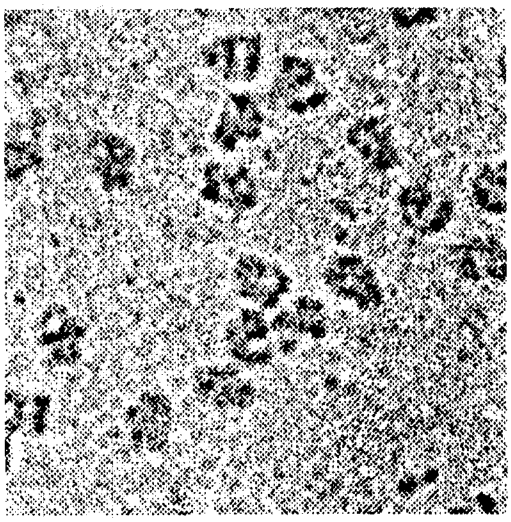

Fig. 1. Cryoelectron microscopy of DNA-PKcs particles. A digital micrograph collected at a magnification of 60,000× and with a defocus value of −1.0 μm. Clear structural features can be discerned even in these raw particle images.

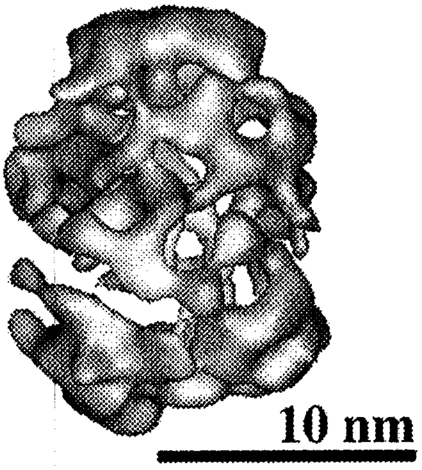

Fig. 2. The cryo-EM image reconstruction filtered to 18-Å resolution. The reconstruction reveals a network of tunnels passing throughout the interior of the protein. One intriguing possibility is that one or more of these tunnels serve as a port of entry for broken DNA ends during the DNA repair process. In order to determine if this is the case, current efforts are directed at determining the structure of the DNA-PK complex with DNA.

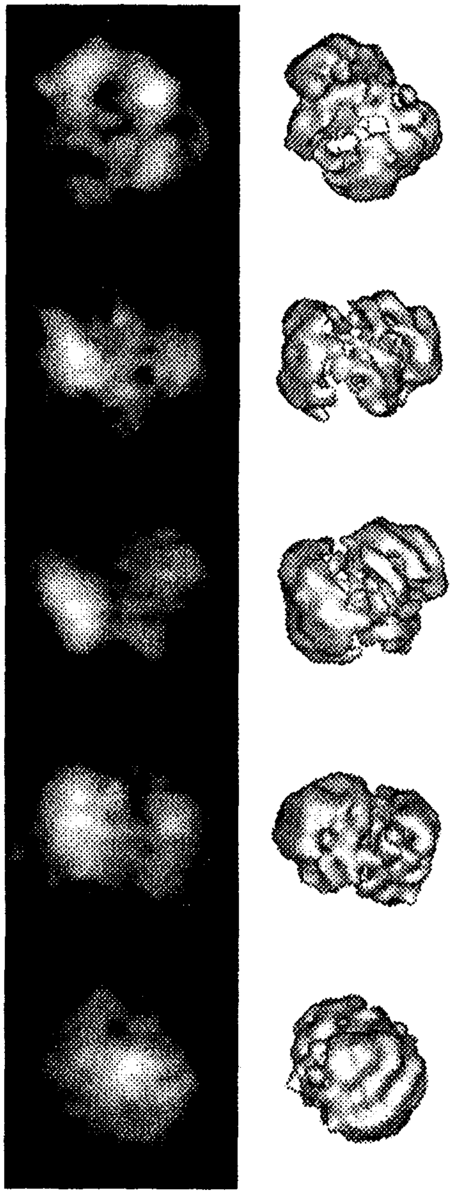

Fig. 3. The three-dimensional structure of DNA-PKcs by two independent structural methods. The cryo-EM derived structure (right column) is based on averaging over 9500 particle images. AFM images (left column) reveal similar structural features without image processing or averaging. The unprocessed, high-resolution AFM particle images were collected in a single scan taking approximately 8 minutes to complete. The speed and resolution of AFM imaging suggests that the microscope will provide a rapid method for determining the three-dimensional structure of large biomolecular complexes.

to validate high-resolution three-dimensional images of single DNA-PK complexes obtained by atomic force microscopy (AFM). AFM technology promises the capability to obtain high-resolution three-dimensional structural information from single macromolecular complexes without the need for image averaging or computationally intensive processing. The further development of AFM technology for imaging of biological specimens at high resolution is a significant outcome of the work funded by this proposal. We have successfully aligned projections of the DNA-PKcs cryo-EM structure with AFM images of DNA-PKcs particles adsorbed to a mica surface collected at Los Alamos. Pairs of aligned images are similar in overall shape and submolecular detail (Fig. 3). This opens up the possibility of rapidly generating three-dimensional models of protein and protein-DNA complexes using AFM-based imaging strategies. The impact of this approach would be far reaching in that it would provide researchers in structural biology and pharmaceutical drug design with a rapid means of characterizing the effects of mutations and drugs on the formation and conformation of critical protein complexes.

Refereed Publications

Chiu, C.Y., R.B. Cary, D.J. Chen, S.R. Peterson, and P.L. Stewart, "Cryo-EM Imaging of the Catalytic Subunit of the DNA-Dependent Protein Kinase," *J. Mol. Biol.* 284, 1075 (1998).

Seitz, E.M., J.P. Brockman, S.J. Sandler, A.J. Clark, and S.C. Kowalczykowski, "RadA Protein Is an Archaeal RecA Protein Homolog That Catalyzes DNA Strand Exchange, *Genes Dev.* 12, 1248 (1998).

Presentations

Seitz, E.M., J. Brockman, S.J. Sandler, A.J. Clark, and S.C. Kowalczykowski, "RadA Protein Is an Archaeal RecA Protein Homolog That Catalyzes DNA Strand Exchange," Federation of American Societies of Experimental Biology Conference on Genetic Recombination and Genomic Rearrangements, Snowmass, CO, August 2–7, 1997 (invited).

Stewart, P.L., "Cryo-EM Imaging of an Integrin; a Ribonucleoprotein Particle; a Small Heat-Shock Protein; and a DNA Repair Enzyme," Laboratory of Structural Biology, NIAMSD, National Institutes of Health, Bethesda, MD, February 27, 1998 (invited).

Stewart, P.L., "Cryo-EM Imaging of an Integrin; a Ribonucleoprotein Particle; a Small Heat-Shock Protein; and a DNA Repair Enzyme," Department of Biochemistry, Univeristy of California, Riverside, CA, May 7, 1998 (invited).

9848

Investigations of Plant Cover Effects on Evaporation and Soil Water Dynamics

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Abstract

The importance of vegetation on global climate change and soil water balance is widely recognized, yet few studies have examined the potential effects of vegetation shifts under controlled experimental conditions over decadal time scales. A set of four unconfined lysimeters in the San Dimas Experi-mental Forest, near Los Angeles, California, provides a unique opportunity to examine the influence of different vegetation covers on soil moisture and percolation under controlled conditions. The lysimeters, 28.1 m^2 by 2.1 m deep, were specifically designed to minimize variation of all environmental conditions except vegetation. They were filled with a fine sandy loam, and steps were taken to reduce inhomogeneities during filling. After an equilibration period of nine years, monocultures of California buckwheat *(Eriogonum fasciculatum)*, chamise *(Adenostoma fasciculatum)*, scrub oak *(Quercus dumosa)*, and Coulter pine *(Pinus Coulteri)* were planted in 1946. These monocultures have been maintained to the present (the pine lysimeter has developed a grass and shrub

understory), allowing an examination of the effects of the vegetation covers resulting from 50 years of growth.

In 1997, two soil cores were collected from each lysimeter. The cores were analyzed for pore-water chloride and stable isotopes (d^{18}O and dD). These natural tracers were used to examine differences in soil water movement between the four vegetation covers. Profiles of pore-water chloride concentrations with depth do not show any obvious differences between vegetation covers. However, the oak profiles have the largest cumulative chloride inventories, suggesting that soil water movement is slower under the oak cover. Chloride concentrations are generally highest in the top 10 cm in all of the profiles, and approximately constant concentrations occur at deeper depths. With the exception of the oak, differences in soil water movement related to the given vegetation covers have apparently been minimal over the 50-year period. One reason that rates of downward soil water movement in the oak profiles may be lower is that the soil A-horizon under the oak has developed distinctly different soil and hydrologic properties. Another possibility is that the interception of precipitation or the evapotranspiration rates in the oak may be higher than in the other covers. Stable isotope and interception data are currently being analyzed to explain why the oak downward flux rates are different from the rest.

By providing quantitative and qualitative information about the role of vegetation type in global change and the hydrologic cycle, this work advances the mission of Los Alamos, UC, and DOE. In addition, understanding vegetation effects on water movement is key to optimizing waste isolation designs such as engineered landfill covers.

Nonrefereed Publication

Newman, B.D., R.C. Graham, J.A. Wald, and K.L. Rose, "Effects of Vegetation Covers on Soil Water Movement Over a 50 Year Period at the San Dimas Experimental Forest, California," *EOS, Trans., Am. Geophys. Union* 79 (45), F259, (November 10, 1998).

Presentation

Newman, B.D., R.C. Graham, J.A. Wald, and K.L. Rose, "Effects of Vegetation Covers on Soil Water Movement Over a 50 Year Period at the San Dimas Experimental Forest, California," Meeting of the American Geophysical Union, San Francisco, CA, December 6–10, 1998 (contributed)

9849
A Mesoscopic Optical Instrument for Detection of TNT

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Graduate Student: Nicolai Kobylk, Department of Electrical and Computer Engineering, UC Davis

Abstract

Miniaturized, smart sensor array systems are needed to address a variety of national security and civilian problems. The need is especially acute for rapid, point detection of chemical or biological agents and in the detection of land mines. Research at Los Alamos has focused primarily on the active sensor element for detection of biological and chemical species using modern molecular recognition approaches in combination with self-assembly. In order to position the Laboratory for future large programs that are aimed at developing integrated smart sensor systems, it is critical to develop a laboratory prototype that can be used in field demonstrations. The sensor module that we are realizing has exchangeable components that make it highly flexible for the development of new sensing instruments, yet it is quite small (1–3 cm dimensions) and robust, with a relatively low manufacturing cost.

The design, fabrication, and testing of a prototype, chemical-sensing module, based on optical detection of the selective adsorption of gas-phase molecules is the subject of this project. The test case species for detection is TNT and other explosives, although the same construct can be applied to many other species, including chemical warfare agents. Selective adsorption is achieved by the attachment of highly sensitive and selective self-assembled monolayers (SAMs) to the surface of thin-film waveguides. Adsorption of the target species produces changes in refractive index, which are detected by a shift in the phase of light traveling in the waveguides. The sensing module is a silicon-based optical breadboard that enables modular assembly and alignment of the planar waveguide and optical fibers. A key feature of the module is that the SAM-coated waveguides can be removed, coated, analyzed in other types of instruments, and reinserted into the sensing module. The research tasks for 1998 were the design, fabrication, and testing of thin-film waveguides at UC Davis; the application and testing of the SAMs on the waveguides at Los Alamos; the design and development of an active alignment scheme (microstage actuation) for the module at UC Davis; and testing of fiber coupling at Los Alamos.

Waveguide fabrication at UC Davis is proceeding, albeit with some difficulty. A waveguide mask layout was designed at UC Davis, and the mask fabrication was attempted using photo pattern generation. However, the high aspect ratio (length to width) of the waveguides requires the mating of many flashes and highly accurate alignment that was not possible with our systems. Therefore, a new mask layout, designed at the University of Arizona, was sent to a commercial mask shop, which generated the mask using a laser system. This mask was used to pattern silicon nitride layers deposited at UC Davis onto oxide-coated silicon wafers. The first waveguides were etched using reactive ion etching. They were tested at Los Alamos and found to transmit one polarization mode (TE) of the laser light with low loss, but the other mode (TM) was not being maintained. Comparison with commercially fabricated waveguides indicate that structurally, the waveguides are the same, but the commercial waveguides have a capping oxide that may be providing the better performance. Fabrication and testing of oxide-coated waveguides is underway.

Application and testing of SAMs on the waveguides have been limited by the lack of availability of waveguides. However, procedures for patterning have been developed. Ultraviolet light is being used to remove the films from selected regions. Photomasks have been designed and fabricated at UC Davis to facilitate this process.

A hybrid module was assembled at UC Davis using two orthogonally mounted, silicon breadboards. The design and mask fabrication for a single, silicon breadboard, with orthogonal dovetailed rails, has been completed, and fabrication is in progress. The hybrid module was assembled by mounting dovetailed sliders on one breadboard that move only in the y-direction. These sliders are used to mount and position the modular waveguides. Dovetailed sliders with x,z positionable stages were mounted on the other breadboard. These carry the optical fibers. The x-position moves the fiber to the edge of the waveguide and the z-motion is for the critical vertical alignment. Bimorph cantilever actuators were mounted onto the breadboard for controlled, active z-position alignment of the fibers to waveguides. Full range of motion of the bimorph cantilever is 100 µm with position accuracy of 0.01 µm. Successful coupling of polarized fibers to the waveguides were recently demonstrated at Los Alamos, using the bimorph cantilevers for z-positioning and manual positioning in x and y. An electrostatic stepping motor for the actuation of the waveguide stage in the y-direction has been designed, and the masks have been generated. Fabrication is underway at UC Davis.

This micromotor will provide ±5-µm indexing of the stage with respect to the fiber core. We expect to demonstrate a prototype motor by June 1999.

Refereed Publications

Grace, K.M., K. Shrouf, S. Honkhanen, P. Aryas, P. Katila, M. Leppihalme, R.G. Johnston, X. Yang, B. Swanson, and N. Peyghambarian, "Waveguide Zeeman Interferometry for Thin-film Chemical Sensors," *Electron. Lett.* 33 (19), 1651 (1997).

Grace, K.M., K. Shrouf, S. Honkanen, P. Ayras, P. Katila, M. Leppihalme, R.G. Johnston, X. Yang, B. Swanson, and N. Peyghambarian, "Thin-Film Chemical Sensors Using Zeeman Waveguide Interferometry," in *Proceedings of the 12th International Conference on Optical Fiber Sensors,* Williamsburg, Virginia, October 1997, Vol. 16, pp. 374–377.

Grace, K.M., B. Swanson, K. Shrouf, S. Honkanen, P. Ayras, P. Katila, M. Leppihalme, R.G. Johnston, X. Yang, and N. Peyghambarian, "Real Time Chemical Detection Using Species Selective Thin Films and Waveguide Zeeman Interferometry," in *Proceedings of the SPIE, Electro-Optical Technology for Chemical Detection and Identification III,* Orlando, FL, April 1998, Vol. 3383, pp. 27–32.

Presentations

Grace, K.M., K. Shrouf, S. Honkanen, P. Ayras, P. Katila, M. Leppihalme, R.G. Johnston, X. Yang, B. Swanson, and N. Peyghambarian, "Thin-Film Chemical

Sensors Using Zeeman Waveguide Interferometry," 12th International Conference on Optical Fiber Sensors, Williamsburg, Virginia, October 1997 (contributed).

Grace,K.M., B. Swanson, K. Shrouf, S. Honkanen, P. Ayras, P. Katila, M. Leppihalme, R.G. Johnston, X. Yang, and N. Peyghambarian, "Real Time Chemical Detection Using Species Selective Thin Films and Waveguide Zeeman Interferometry," SPIE, Electro-Optical Technology for Chemical Detection and Identification III, Orlando, FL, April 1998 (contributed).

9857

Magnetic Quadrupole–Induced Resonant Particle Transport in a Pure Electron Plasma

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Abstract

We have performed experiments that demonstrate the effects that a transverse quadrupole magnetic field has on a pure electron plasma confined in a Malmberg-Penning trap. The confinement of charged particles within a Malmberg-Penning trap depends mostly on the uniformity of the axial magnetic field. If the cylindrical symmetry is broken, we generically expect the confinement to be degraded. However, detailed mechanisms particular to a given asymmetry are not well understood.

This research has two goals. First, understanding the effects of the quadrupole magnetic field on plasma lifetimes will help to establish whether or not they can be successfully used in experiments to create and confine antihydrogen. Second, we believe the plasma is lost through a resonant particle transport effect. Direct observation of resonant particle transport is an important goal in the field of nonneutral plasma physics.

In our experiments, we have applied a transverse quadrupole magnetic field and measured the resulting decrease in confinement time. The shape of the plasma has been explored. Without quadrupole fields, the plasma is cylindrical. When the

quadrupole field is applied, the cross section becomes elliptical. We have also seen the resonant nature of this effect by observing enhanced transport at a certain combination of parameters and lesser transport as we move away from these parameter values. This is important because it suggests that the addition of quadrupole fields to a Malmberg-Penning trap need not render the trap useless.

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BooNE Collaboration

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Abstract

Evidence for neutrino mass oscillations has been presented by the Liquid Scintillating Neutrino Detector (LSND) Collaboration from data collected at the Los Alamos Neutron Science Center. Both neutrino and antineutrino oscillations have been observed, and have consistent mixing parameters within the limited systematics and statistics of the LSND project.
A collaboration of scientists from Los Alamos National Laboratory, Fermi National Accelerator Laboratory (Fermilab), and several universities presented a proposal to Fermilab to confirm and measure the characteristics of these mass oscillations with at least an order-of-magnitude higher statistics. This new project—BooNE, for the Booster Neutrino Experiment—has been approved and will use a new neutrino source associated with the FermiLab 8-GeV booster proton

synchrotron. Construction of the experiment will begin by the end of 1999 and data-taking should commence by the end of 2001.

Nonrefereed Publications

Church, E., I. Stancu, G.J. VanDalen, R.A. Johnson, et al., "A Proposal for an Experiment to Measure n_μ to n_e Oscillations and n_μ Disappearance at the Fermilab Booster (BooNE)," FERMILAB-P-0898; Los Alamos National Laboratory document LA-UR-98-352 (January 15, 1998).

Stancu, I., et al., "Evidence for Neutrino Oscillations from LSND: Past, Present and Future," in *Proceedings of the Second International Workshop on the Identification of Dark Matter*, Buxton, England, September 7–11, 1998.

Presentation

Stancu, Ion, "Evidence for Neutrino Oscillations from LSND: Past, Present and Future", International Workshop on the Identification of Dark Matter, Buxton, England, September 1998 (invited).

9859

Satellite Imaging Spectrometry

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Undergraduate Student: Khoung James Dihn,
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Abstract

A research collaboration between Los Alamos and UC Santa Barbara was initiated to develop capabilities in the analysis of hyperspectral imaging data. Imaging spectrometry, which provides a near contiguous sampling of the electromagnetic spectrum, is a new technology that may significantly contribute to our ability to detect and map trace chemical substances in the land, water, and atmosphere using airborne or spaceborne instruments. These capabilities are expected to be invaluable as tools for the detection and mapping of environmental contaminants derived from industrial and natural sources or as byproducts from the production of biological, chemical, or nuclear weapons. The tools we are developing for analyzing imaging spectrometry data are expected

to contribute significantly to the environmental sciences and DOE by developing methods for early detection of pollution or proliferation attempts. Furthermore, new developments in the analysis of thermal imaging spectrometry data will contribute significantly to basic research in thermal remote sensing while building expertise in this area within the Univesity of California. New sensors, such as ASTER, which is scheduled to launch in 1999, will require expertise in this field to put the data to full use. Through this research, we are well positioned to use ASTER and other imaging spectrometers as they become available.

Our research partnership in 1998 concentrated on two fundamental problems associated with thermal hyperspectral imaging: unmixing the thermal data to retrieve surface temperature and map surface constituents and removing the "clutter" associated with a heterogeneous background to improve detection of trace atmospheric gasses.

The first objective is commonly termed temperature emissivity separation, in which the effect of temperature on emitted electromagnetic radiation (described by a Planck function) must be separated from the effects of spectral emissivity (a measure of the efficiency at which a material emits radiation relative to a perfect emitter), which also modifies emission. Because both temperature and emissivity control surface radiance, it is necessary to separate the effects of these two factors to identify surface materials and estimate their temperature.

In 1998 we developed a two-stage methodology for mapping surface temperature and surface materials from hyperspectral data. In the first stage, temperature is retrieved using a linear mixing model, in which an endmember called "virtual cold" is used to account for changes in radiance that are due to temperature (Fig. 1). This relationship, while nonlinear, can be linearized through the use of a look-up table between virtual cold fraction and temperature (Fig. 2). Once temperature has been constrained, surface constituents can be identified and mapped by using "isothermal" unmixing, assuming that all materials within the instantaneous field of view of the instrument are at the same temperature (Fig. 3). The method was developed and tested using synthetic hyperspectral images covering a temperature range between 280 and 350 K for 10 materials derived from the ASTER spectral library at the Jet Propulsion Laboratory. In order to test the method on a more realistic scenario, a simulated scene containing a smoke stack, trees, shadows, roof materials, and a plume developed at LANL was unmixed and tested against known temperatures and materials.

The second major focus was on removing background clutter to enhance the capability of detecting a trace atmospheric signal. Here, measured radiance is modeled as a product of the radiance from the background, an atmospheric signature imposed on the background radiance and error. In order to remove clutter due to a heterogeneous background, a k-means clustering algorithm was employed to divide the background into a series of "uniform" clusters or classes. Once the classes are identified, spectral variation caused by surface components can be reduced, leaving a residual spectrum composed of the signal of interest and error. A matched filter was used to map spectral residuals matching specific atmospheric constituents. Initial tests focused on locating a sulfur dioxide plume in a simulated scene.

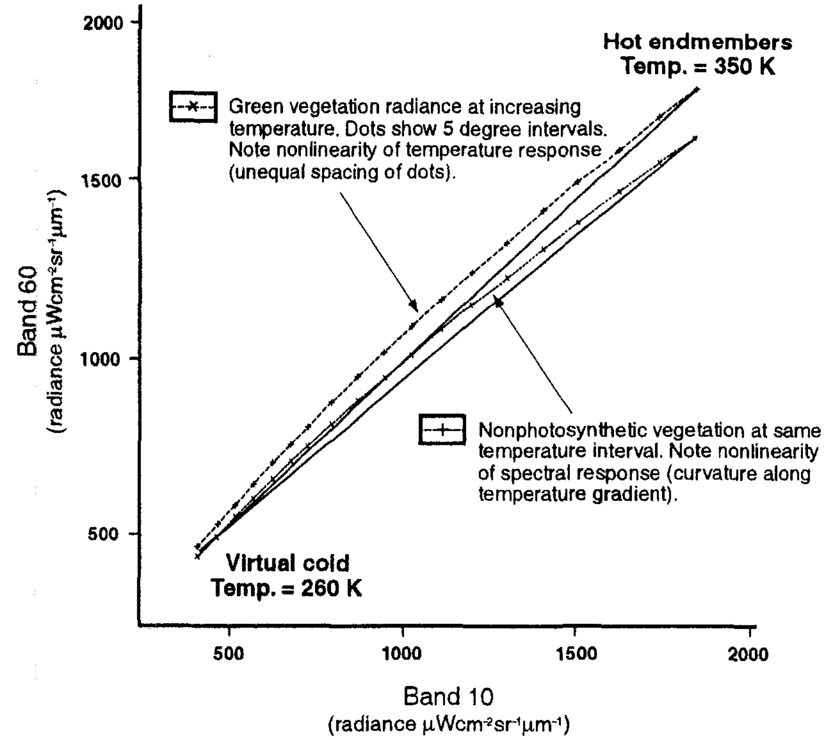


Fig. 1. The predominantly linear nature of the relationship between temperature and radiance for all 10 materials. The relationship is somewhat nonlinear from one band to the next because emission does not increase uniformly across the spectrum as the temperature changes. These deviations from linearity cannot be captured. Nonlinearity with respect to temperature described by Planck's equation can be incorporated into the look-up table. The conclusion is that temperature dominates emission.

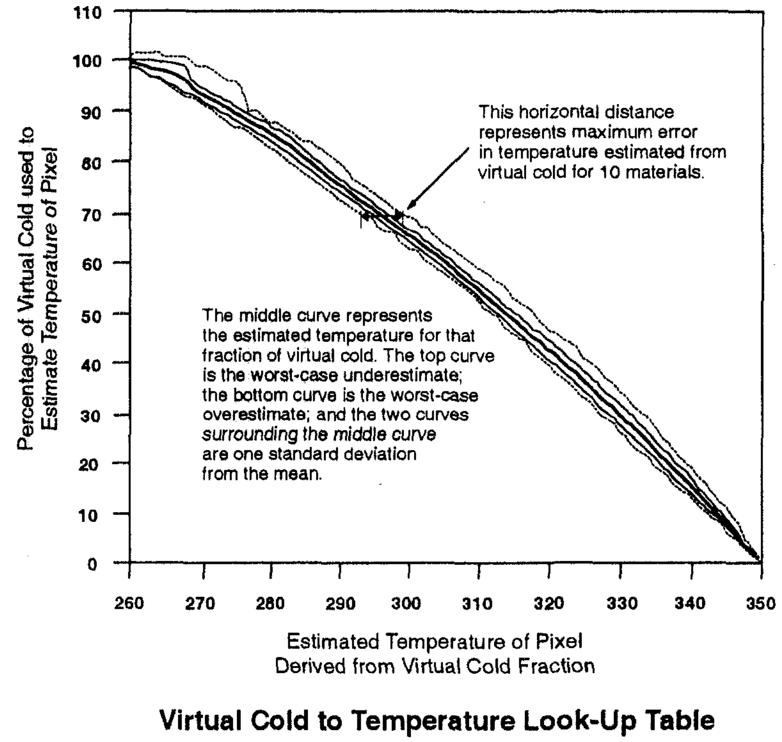


Fig. 2. Because temperature dominates at sensor radiance, spectral mixture analysis can be implemented to estimate a virtual cold fraction of each pixel in the image. This virtual cold fraction is in essence a proxy measure of the average temperature of the pixel. This figure shows how well the virtual cold to temperature look-up table performs on ten classes of material. The conclusion is that the look-up table provides a reasonable estimate of temperature for a mixed pixel.

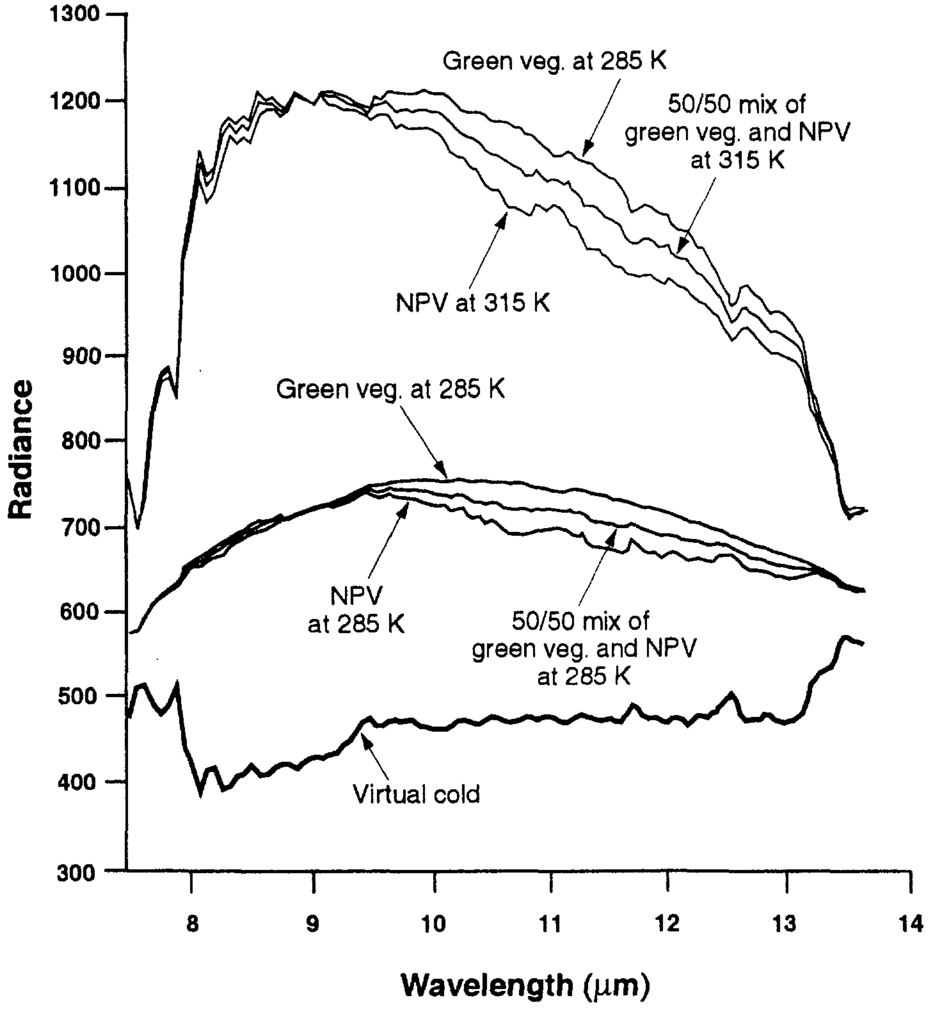


Fig. 3. Once an initial temperature estimate is obtained for each pixel, multiple endmember spectral mixture analysis can be used to isothermally unmix each pixel for two or three endmembers. The conclusion is that once temperature is constrained, compositional information can be obtained.

Nonrefereed Publications

Borel, C.C., "Surface Emissivity and Temperature Retrieval for a Hyperspectral System," in *Proceedings of the International Geoscience and Remote Sensing Symposium (IGARSS '98)* (IEEE, Piscataway, NJ, 1998).

Borel, C.C., W.B. Clodius, and P.V. Villeneuve, "Synthetic Hyperspectral Data Cubes for Complex Thermal Scenes," in *Imaging Spectometry IV*, Michael R. Decour and Sylvia S. Shen, Eds. (SPIE, Bellingham, WA, 1998), Vol. 3438, pp. 222-228.

Painter, T.H., D.A. Roberts, J. Dozier, and R.O. Green, "Automated Subpixel Snow Parameter Mapping with AVIRIS Data," in *Proceedings of the 7th AVIRIS Earth Science Workshop* (Jet Propulsion Laboratory, Pasadena, CA, in press).

Roberts, D.A., K.J. Brown, R. Green, S. Ustin, and T. Hinckley, "Investigating the Relationship between Liquid Water and Leaf Area in Clonal Populus," in *Proceedings of the 7th AVIRIS Earth Science Workshop* (Jet Propulsion Laboratory, Pasadena, CA, in press).

Roberts, D.A., M. Gardner, J. Regelbrugge, D. Pedreros, and S. Ustin, "Mapping the Distribution of Wildfire Fuels Using AVIRIS in the Santa Monica Mountains," in *Proceedings of the 7th AVIRIS Earth Science Workshop* (Jet Propulsion Laboratory, Pasadena, CA, in press).

Presentations

Borel, C.C., W.B. Clodius, and P.V. Villeneuve, "Synthetic Hyperspectral Data Cubes for Complex Thermal Scenes," Meeting of the International Society for Optical Engineering SPIE '98, San Diego, CA, July 19–24, 1998 (contributed).

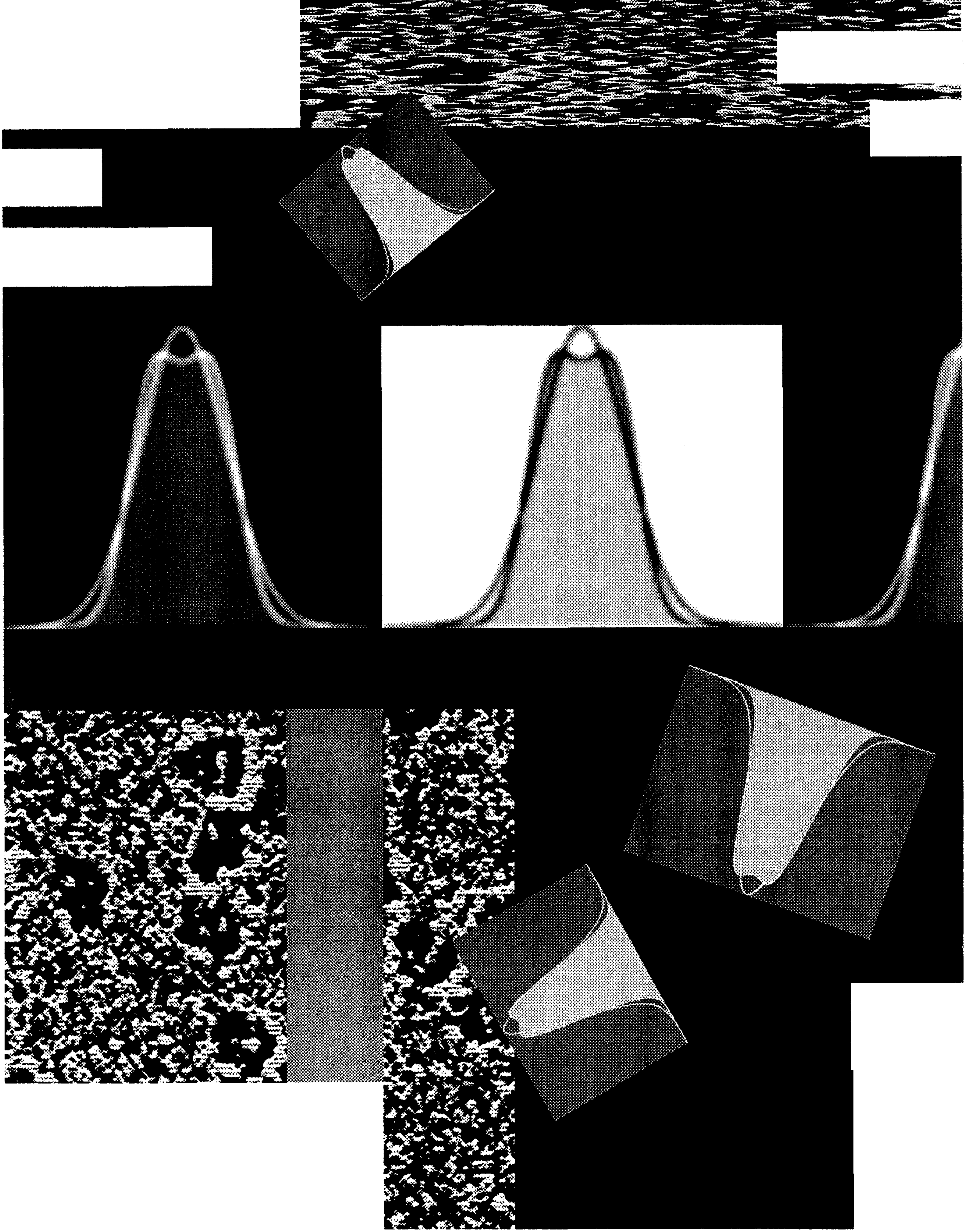
Borel, C.C., "Surface Emissivity and Temperature Retrieval for a Hyperspectral System," Meeting of the International Geoscience and Remote Sensing Symposium, Seattle, WA, July 6–10, 1998 (contributed).

Painter, T.H., D.A. Roberts, J. Dozier, and R.O. Green, "Automated Subpixel Snow Parameter Mapping with AVIRIS Data," 7th AVIRIS Earth Science Workshop, Pasadena, CA, January 12–14, 1998 (contributed).

Roberts, D.A., "Advanced Vegetation Analysis using Imaging Spectrometry," 9th Brazilian Remote Sensing Symposium, Santos, Brazil, September 9–16, 1998 (invited).

Roberts, D.A., K.J. Brown, R. Green, S. Ustin, and T. Hinckley, "Investigating the Relationship between Liquid Water and Leaf Area in Clonal Populus," 7th AVIRIS Earth Science Workshop, Pasadena, CA, January 12–14, 1998 (contributed).

Roberts, D.A., M. Gardner, J. Regelbrugge, D. Pedreros, and S. Ustin, "Mapping the Distribution of Wildfire Fuels Using AVIRIS in the Santa Monica Mountains," 7th AVIRIS Earth Science Workshop, Pasadena, CA, January 12–14, 1998 (contributed).



New Mexico Universities Collaborative Research (NUCOR) Program Progress Reports

The NUCOR Program funds joint Los Alamos National Laboratory–New Mexico campus research projects that enhance the Laboratory's competencies in selected areas and, at the same time, strengthen the technical ties between the Laboratory and the New Mexico campuses. The campuses that participate in this program are the University of New Mexico, New Mexico State University, New Mexico Highlands University, and New Mexico Institute of Mining and Technology. Research projects are collaborative in nature and build on the complementary capabilities and research facilities of the Laboratory and the campuses involved. A goal of the program is to allow campus participants to become more familiar with Los Alamos capabilities and facilities. The research projects are proposed jointly by Los Alamos and New Mexico campus investigators. Work is performed over a period of up to three years; however, funding is approved for only one year at a time. Depending on the requirements, funding for each project can be as much as $55,000 per year. Most of this funding is spent at the participating campus, but at least $5000 of the funding must be spent at Los Alamos. Each participating New Mexico campus may submit up to four new proposals to Los Alamos each year, with the campus research administrator determining how the proposals are selected at the campus. The proposals undergo peer review by Los Alamos committees for the major technical focus areas. There is a yearly call for NUCOR proposals. Additional details of the program are given in the call for NUCOR Program proposals, which is available on the World Wide Web at http://stb.lanl.gov/uc.

Sixteen NUCOR proposals were submitted to Los Alamos by the four New Mexico campuses, and four new proposals were selected for FY 1998 funding. One proposal failed to mature. These collaborations fall within three focus areas that match the Laboratory's core competencies in earth and environmental systems, materials, and satellite and remote sensing.

Three NUCOR project reports, with listings of personnel, publications, presentations, patents, and awards for FY 1998 follow in this section.

Contents

Abstracts

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Plate Tectonics and Three-Dimensional Spherical Models of Mantle Convection with Brittle Lithosphere

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Abstract

Why does Earth have plate tectonics instead of being covered by a stagnant lithosphere like that on Mars or Venus? Many researchers have recognized that the answer probably lies in the complicated mechanical behavior of rocks. Rocks can slowly creep in a manner resembling fluid flow. However, their viscosity is unlike ordinary fluids in that it is nonlinear and depends on many factors such as temperature, pressure, and deformation rate. On the other hand, rocks are solids and therefore can fracture. Plate tectonics, we suspect, is a consequence of this complicated mixture of fluid and solid properties of rocks. This is the basic motivation for our efforts in numerical and theoretical modeling of mantle convection. The models described in the papers published during the last year take into account these mechanical complexities of rock behavior. They develop further the concept of stagnant lid convection on the terrestrial planets and demonstrate how extremely inefficient heat transport is on planets that do not have plate tectonics. In this context we advanced the idea of magmatic resurfacing of Venus as an alternative explanation for its global resurfacing. We showed, at least qualitatively, how plate tectonics on Earth and Venus could initiate and stop as a result of the complicated mixture of fluid and solid properties of rocks.

Convection with realistic rock behavior has been studied in three dimensions as well. We bench-marked the Los Alamos three-dimensional (3-D) code TERRA. The accuracy of the current simulations turns out to be around 2% to 3%. TERRA was applied to systematic investigation of stagnant lid convection in a spherical shell. The scaling laws obtained show a surprising similarity with two-dimensional convection and theory. Currently, we are concentrating our efforts on the 3-D simulations of both stagnant lid convection and plate tectonics. Important results can be obtained in a relatively short period of time thanks to excellent computing facilities, which now include eight Sun Ultras at New Mexico State University and powerful supercomputers at Los Alamos and the Jet Propulsion Laboratory at the California Institute of Technology. (Those are used for high-resolution 3-D runs carefully chosen from lower resolution cases.) In addition, TERRA has been recently modified by implementing a new particle method for tracking the positions of lithospheric plates and adding yield stress criterion for brittle fracture.

This resulted in a substantial improvement in the description of plate motion and mantle circulation.

The results we have obtained have important implications for understanding planetary evolution. It is becoming more and more apparent that Earth and other planets have not been simply cooling down with time as suggested by previous less detailed models. The evolution of these bodies is likely in most cases to have been quite violent, with early episode(s) of plate tectonics and later episode(s) of intense magmatism. The goal of this research is eventually to account for the past and present day tectonics of Earth and other planets in terms of their initial conditions, size, surface temperature, presence of water, and other factors that affect the mechanical properties of rocks in various complex ways.

Refereed Publications

Bunge, H.-P., M.A. Richards, C. Lithgow-Bertelloni, J.R. Baumgardner, S.P. Grand, and B.A. Romanowicz, "Time Scales and Heterogeneity Structure in Geodynamic Earth Models," *Science* **280**, 91 (1998).

Moresi, L.-N., and V S. Solomatov, "Mantle Convection with a Brittle Lithosphere: Thoughts on the Global Tectonic Style of the Earth and Venus," *Geophys. J.* **133**, 669 (1998).

Reese, C.C., V.S. Solomatov, and L.-N. Moresi, "Heat Transport Efficiency of Stagnant Lid Convection with Dislocation Viscosity: Application to Mars and Venus," *J. Geophys. Res.* **103**, 13643 (1998).

Reese, C.C., V.S. Solomatov, and L.-N. Moresi, "Non-Newtonian Stagnant Lid Convection and Magmatic Resurfacing of Venus" (to be published in *Icarus*).

Reese, C.C., V.S. Solomatov, J. Baumgardner and W. Yang, "Stagnant Lid Convection in a Spherical Shell" (submitted to *Geophys. Res. Lett.*).

Presentations

Baumgardner, J., M.A. Richards, W. Yang, and C.R. Lithgow-Bertelloni, "3-D Spherical Models of Plate Motion with Laterally Varying Rheology," Meeting of the American Geophysical Union, San Francisco, CA, December 6–10, 1998 (contributed).

Moresi, L.-N., A. Lenardic, S. Solomatov, and H. Muhlhaus, "On the Survival of Cratons in a Vigorously Convecting Mantle," 22nd International Conference on Mathematical Geophysics, Cambridge, U.K., 1998 (contributed).

Reese, C.C., V.S. Solomatov, and L.-N. Moresi, "Non-Newtonian Stagnant Lid Convection: Application to Mars," 29th Lunar and Planetary Science Conference, March 16–20, 1998 (contributed).

Reese, C.C., V. S. Solomatov, and L.-N. Moresi, "Non-Newtonian Stagnant Lid Convection and Magmatic Resurfacing of Venus," Meeting of the American Geophysical Union, San Francisco, CA, December 6–10, 1998 (contributed).

Solomatov, V.S., F. Bakalian, and L.-N. Moresi, "Numerical Simulations of the Transition from Plate Tectonics to Stagnant Lid Convection: Application to Global Resurfacing on Venus," 29th Lunar and Planetary Science Conference, March 16–20, 1998 (contributed).

Solomatov, S.V., F. Bakalian, C.C. Reese, and L.-N. Moresi, "Numerical Simulations of Mantle Dynamics and Evolution with Brittle Lithosphere," 22nd International Conference on Mathematical Geophysics, Cambridge, U.K., 1998 (contributed).

Yang, W., and J. Baumgardner, "Mantle Avalanches as a Consequence of Non-Linear Rheology," Meeting of the American Geophysical Union, San Francisco, CA, December 6–10, 1998 (contributed).

9873

Optical Refrigeration in Semiconductors

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Undergraduate Student: Frank Wippermann, Fachhochschule Jena, Germany

Abstract

It was proposed to investigate optical refrigeration in glasses and semiconductors. Optical refrigeration operates on the principle that certain materials absorb laser light at one wavelength and subsequently fluoresce at a shorter wavelength, thereby removing heat from the system. This research would draw on the strength in semiconductor materials and optical physics at the University of New Mexico (UNM) and on established experience in glass-based optical refrigeration at Los Alamos National Laboratory. The development of all-solid-state optical refrigerators by the collaboration between UNM and Los Alamos could have profound effects on cooled electronics. This development should make it possible to have integrated coolers with

electronic devices such as infrared sensors or high-temperature superconductors (possibly even low-temperature superconductors). These devices have great potential for satellite-borne and ground-based applications of interest to government and commercial organizations.

The recent laboratory work and computer simulations indicate that a practical, first generation, all-solid-state fluorescent cryocooler will have the following properties:

- no vibrations,
- no production of or susceptibility to electromagnetic interference,
- cool to 77 K,
- ≈1% efficient (DC power to cooling power), and
- lifetime of 10 years of continuous operation.

The Los Alamos team has already demonstrated net differential cooling of ≈16 degrees from room temperature in Yb^{+3}-doped ZBLANP optical fibers. The challenge is to demonstrate the scaling of the cooling process to higher powers toward achieving cryogenic temperatures. These challenges, however, differ in complexity, depending on the cooling material that is used. The following main tasks are considered as a systematic approach toward producing efficient all-solid-state laser cryocoolers.

Time resolved and power scaling study on ytterbium-doped systems. To probe the details of underlying physics, we need to conduct a rigorous study of the dynamics of the cooling process. For this reason we have designed and developed a new pulsed-laser source based on optical parametric oscillation. This system is operational, and after minor refinement to stabilize its wavelengths, we will start conducting a series of time-resolved spectroscopy experiments on the ytterbium-doped glasses. The UNM team collaborated also with the University of St. Andrews in Scotland in building the aforementioned laser system.

Cooling feasibility study on thulium-doped materials. Simple analysis indicates that the cooling efficiency scales with the mean fluorescence wavelength λ_F. Thus, materials whose active dopants absorb and emit at longer wavelengths offer greater efficiency. Among immediate candidates are thulium-doped glasses with transitions in the λ=2 μm region, offering an efficiency increase by a factor of 2 over ytterbium-doped systems. In addition to better efficiency, another possible advantage at this stage is the availability—or ease of production—of high-power tunable sources at λ=2 μm. We have designed, ordered parts for, and are currently constructing a high-power OPO system using periodically polled lithium niobate pumped by a high-power continuous-wave YAG laser at UNM.

Investigation of semiconductor heterostructures for laser refrigeration. Although the theoretical and preliminary experimental studies suggest that these materials may have great value, there are some outstanding, unresolved issues. To cool effectively, the semiconductor has to have a total (or external) quantum efficiency of at least 98%. That is, nearly all the light that is absorbed by the semiconductor must be reemitted and escape without producing heat. Although it has been shown that "internal" quantum efficiency exceeds 99% (in a single absorption little heat is generated), light tends to be trapped in semiconductors and reabsorbed many times. Our objectives are to obtain uniform and pure semiconductor material with high internal quantum efficiencies and to develop novel heterostructures that have relatively little light trapping and hence high external quantum efficiencies. In collaboration with the UNM Center for High Technology Materials, we have designed a number of GaAs-based structures that are promising in producing high external efficiency.

Refereed Publications

Edwards, B.C., M.I. Buchwald, and R.I. Epstein, "Development of the Los Alamos Solid-State Optical Refrigerator," *Rev. Sci. Instrum.* 69, 2050 (1998).

Lei, G., J.E. Anderson, M.I. Buchwald, B.C. Edwards, R.I. Epstein, M.T. Murtagh, and G.H. Sigel, "Spectroscopic Evaluation of Yb^{3+}-Doped Glasses for Optical Refrigeration," *IEEE J. Quantum Electron.* 34 (10), 1839 (1998).

Presentation

Hoyt, Chad, "Optical Refrigeration in Solids," Optics Seminars, Department of Physics and Astronomy, University of New Mexico, Albuquerque, 1998.

9874

Novel Beacons for Adaptive Optics

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Abstract

Adaptive optics—the technique of sensing distortions and correcting them—is used for real-time correction of image distortions caused by atmospheric turbulence. The technique requires a point source close to the object of interest. A telescope mirror is deformed to minimize the size of the image of the reference point, which implies that the optics has compensated for atmospheric distortion. This project addresses the problem of creating a distant point source through laser excitation for the corrected viewing of stars, planets, and satellites. Present state of the art is to excite with resonant radiation the D_2 transition of sodium in Earth's mesospheric layer to create an artificial beacon at an altitude of approximately 90 km. There are three basic problems with that approach: (a) the monochromatic radiation propagates twice through the same path in the atmosphere and therefore cannot correct the lowest order ("tip-tilt") wavefront perturbations; (b) because a single-photon transition is used, low-power (nonsaturating) radiation has to be used to prevent loss by reemission in the forward direction; and (c) the low density of sodium

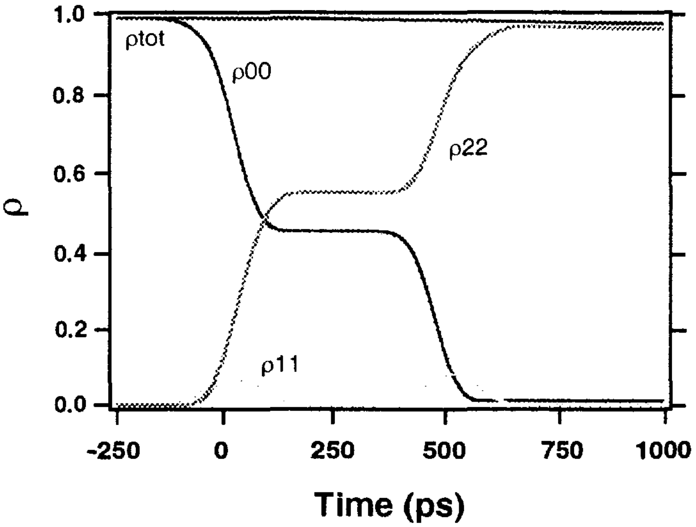


Fig. 1. The graph shows the results of a computer simulation, solving the Optical Bloch Equations for a three-level system for sodium. This is a valid approxi-mation due to large inhomogenous broadening. The simulation took relaxation into account and shows clearly how nearly all the population can be transferred from the lowest level (3s: ρ00) into the upper level (4s: ρ22). The pulse sequence is separated by 500 ps, and it can be seen that even though there is minimal population transfer into and from the intermediate level (3p: ρ11), it is left unpopulated after the pulse sequence.

(10^4 atoms/cm^3) puts a fundamental limit to the maximum return that can be achieved. We offer a solution to the first two problems by exploiting properties of two-photon resonant coherent interaction in sodium. We intend to solve the third problem through multiphoton excitation of the most abundant components of the atmosphere: molecular oxygen and nitrogen and atomic oxygen.

Our computer simulations have recently demonstrated that a two-colored pulse sequence can be used to coherently excite the sodium 3s-4s transition. Figure 1 shows that a complete population inversion is achieved in a two-step process after excitation by a pair of bichromatic pulses of less than 1 μJ/cm^2 energy. Figure 2 shows that the resultant excitation of the 4s level is nearly complete over the full width at half maximum of a Gaussian beam of appropriate peak intensity. From that upper level, there is an isotropic probability of emission of 1.4 μ and 589 nm, cascading down to the lowest level. Even at a high repetition rate, the power levels, required for the two-photon bichromatic coherent excitation, are very moderate—about several watts and therefore easily achievable with present technology. This approach could revolutionalize adaptive optics and could make it truly practicable and achievable even for satellite tracking.

Because of the complicated nature of the subject (complicated atomic structure and propagation issues in the atmosphere), more elaborate computer simulations are required to accurately fit the experimental data and scale the results to the mesospheric conditions. For the experimental part, the cascade of nonlinear processes (frequency doubling, single-pulse extraction and amplification, synchronously pumped optical parametric

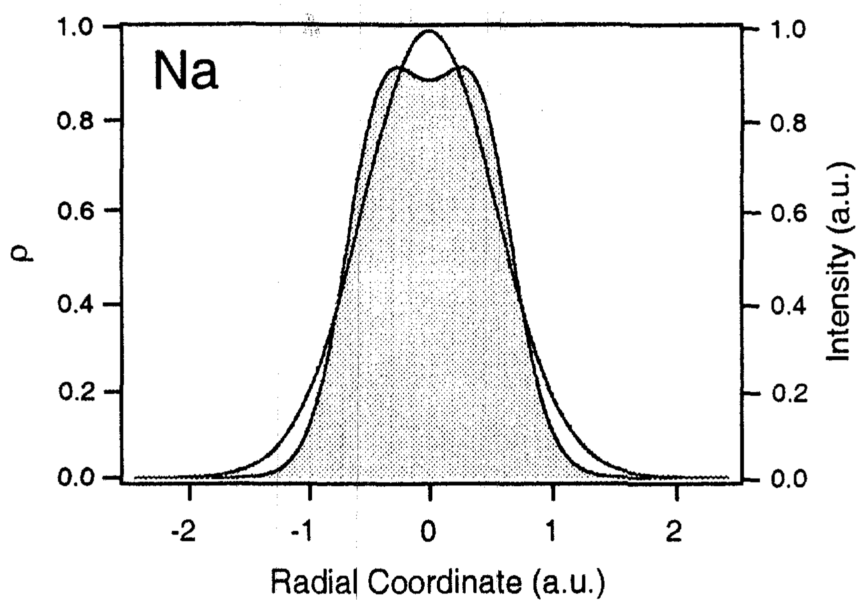


Fig. 2. The single-peak curve is the spatial intensity profile of the laser pulse as a function of the radial coordinate. The gray area indicates a slice through the volume of coherently excited sodium atoms.

oscillator, followed by a parametric amplifier, frequency doubling and sum frequency generation) has been successfully tested at the University of New Mexico on a prototype generating picosecond pulses at 248 nm. The same set of components is now being reassembled to generate the pair of bichromatic pulses for coherent pumping of sodium.

Investigation of the multiphoton absorption cross sections of various molecular species has already started with measurements of two-, three-, and four-photon ionization of NO, O_2, and N_2 at 248 nm. Extension of these measurements to multiphoton absorption and fluorescence of these species with a combination of wavelengths is planned for 1999.

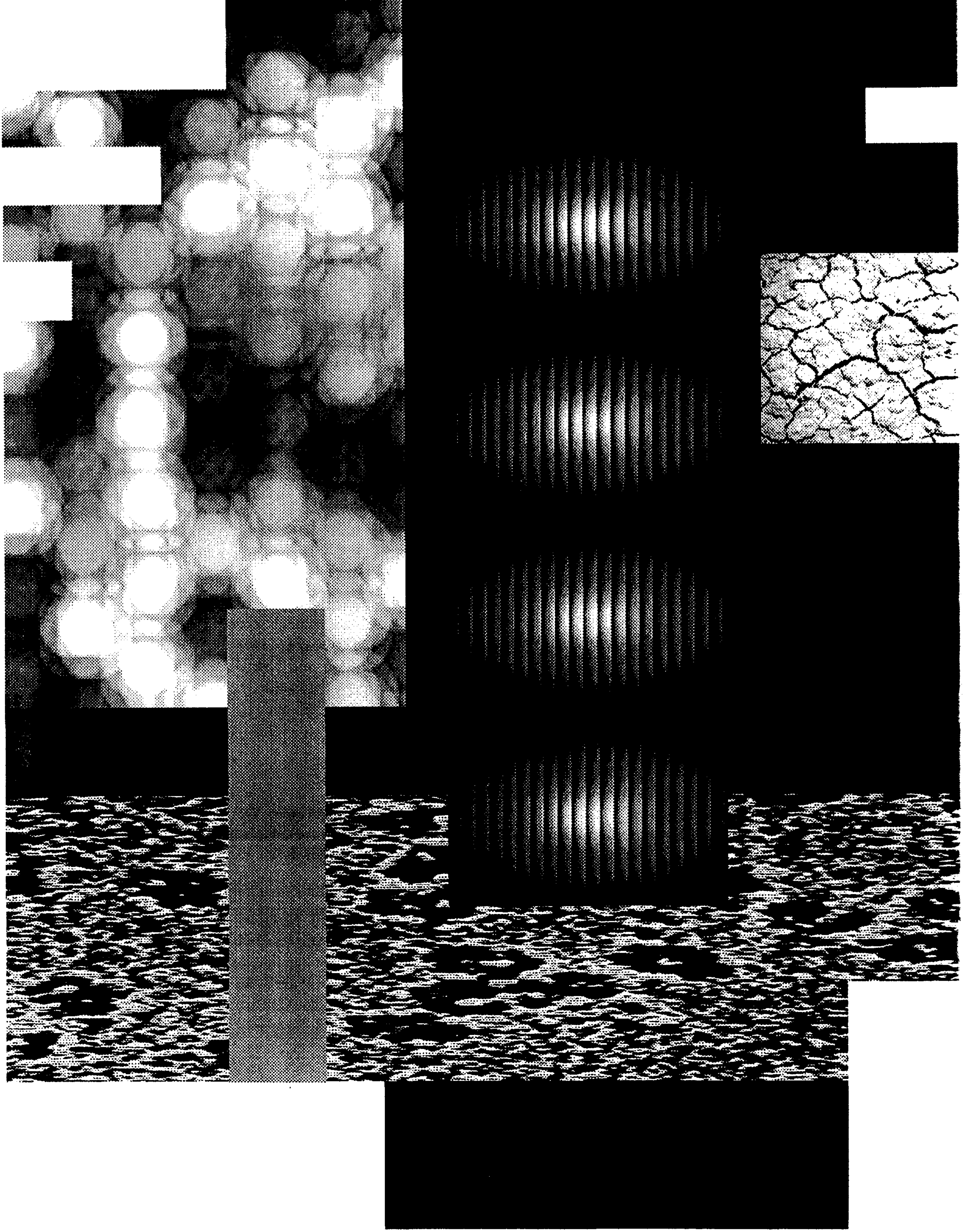
Refereed Publication

Diels, J.-C., J. Biegert, and J. McGraw, "Alternatives to the Conventional Sodium Beacon," in *Adaptive Optics and Optical Interferometry,"* Bill Junor, Sergio Restaino, and Neb Duric, Eds. (Astronomical Society of the Pacific, San Francisco, in press), Conf. Ser.

Presentations

Diels, J.-C., "Beacons for Adaptive Optics," Physics Colloquium, Technische Universitat München, München, Germany, February 1998 (invited).

Diels, J.-C., J. Biegert, and J. McGraw, "Alternatives to the Conventional Sodium Beacon," Astronomical Society of the Pacific Conference Series: Catching the Perfect Wave—Adaptive Optics and Interferometry in the 21st Century, Albuquerque, NM, June 28–July 1, 1998 (contributed),



New Mexico Research Partnership Initiative (NMRPI) Progress Reports

NMRPIs use UCDRD funds to foster the development of joint research activities and capabilities that are of strategic interest to Los Alamos National Laboratory and that have the potential for external funding. The goal is to strengthen activities so that they can become self-sustaining through external funding. No formal call for proposals is issued. Proposals are submitted to the UC Coordination Office at Los Alamos, which makes recommendations to the Laboratory Director. As funds become available, proposals are selected from those that have been received. Priority is given to those projects that strengthen the strategic directions and core competencies of the Laboratory and that result in establishing or strengthening important collaborations. Additional details of the program are available at on the World Wide Web at http://stb.lanl.gov/uc.

Seven new NMRPIs were funded in FY 1998. Two project reports, with listings of personnel, publications, patents, and awards for FY 1998 follow in this section.

Contents

Abstracts

9871

Porosity Prediction Using Three-Dimensional Seismic Data, Permian Basin

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Additional Collaborator: Harvey E. Yates Company, Roswell, New Mexico

Graduate Student: Robin Pearson,
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Abstract

Three-dimensional-seismic, log, and production data from the Bone Spring Formation of southeast New Mexico constitute a remarkable data set with which to examine the relationships between seismic attributes and reservoir properties. Seismic attributes can be thought of as quantitative descriptions of specific aspects (e.g., amplitude, frequency, and phase) of the reflected energy that is recorded from subsurface interfaces such as those that exist between different rock formations.

We established a research team that investigated these relationships using a study that integrated geology, geophysics, geostatistics, and computer visualization. We sought to develop and publicly document a methodology for deriving physical property (e.g., porosity) volumes from three-dimensional (3-D) seismic data. Our methodology involved the following tasks: (a) identifying and mapping the principal stratigraphic elements using seismic and log data, (b) using log-based methodologies for deriving physical properties of porous units, (c) deriving relationships between seismic attributes and porosity that allowed us to map those properties away from well control, and (d) testing and comparing our results by integrating them with our geologic model and production data from the study area.

The Second Sand of the Bone Spring Formation in our study area represents a slope fan deposit that formed along the flank of a carbonate platform in Permian time (approximately 260 million years ago). From our analyses, it appears that porous intervals in the Second Sand form curvilinear trends that probably represent the axes of submarine channel systems. These trends correspond to the best producing wells in the interval, and the congruence of geophysical, geologic, and production data strengthens the level of confidence in our results. Current work in this area is mostly geared toward examining horizons that are extracted from seismic data. Our efforts have focused on extending this approach to investigate volumes. The results of this study are expected to have an impact on the petroleum industry, academic research, and, potentially, the environmental sector. This work has helped to strengthen the scientific links between the petroleum research groups at Los Alamos National Laboratory and New Mexico Institute of Mining and Technology.

Nonrefereed Publications

Pearson, R.A., "Stratigraphy and Seismic-Guided Estimation of Log Properties of the Second Sand Member of the Bone Spring Formation, Delaware Basin, New Mexico," M.S. thesis, New Mexico Institute of Mining and Technology (submitted).

Pearson, R.A., and B.S. Hart, "Stratigraphy and Seismic-Guided Estimation of Log Properties of the Second Sand Member of the Bone Spring

Formation, Delaware Basin, New Mexico," in *The Search Continues into the 21st Century*, W.D. DeMis and M.K. Nelis, Eds., West Texas Geological Society publication 98-105 (1998), pp. 213–219.

Presentations

Pearson, R.A., and B.S. Hart, "Sequence Stratigraphy and Seismic Attribute Analysis of the Bone Spring Formation, Delaware Basin, NM," Meeting of the New Mexico Geological Society, Socorro, NM, April 9, 1998 (contributed).

Pearson, R.A., and B.S. Hart, "Stratigraphy and Seismic-Guided Estimation of Log Properties of the Second Sand Member of the Bone Spring Formation, Delaware Basin, New Mexico," West Texas Geological Society Fall Symposium, Midland, TX, October 29–30, 1998 (contributed).

Pearson, R.A., and B.S. Hart, "Stratigraphy and Seismic-Guided Estimation of Log Properties of the Second Sand Member of the Bone Spring Formation, Delaware Basin, New Mexico," Roswell Geological Society, Roswell, NM, November 10, 1998 (invited).

9876
Analysis of Implementations of Quantum Computation

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Abstract

Recent advances in quantum information science presage a technological revolution. Heretofore, scientists and engineers have designed systems that, though they use quantum "effects," perform information-processing tasks that can be formulated and described in the language of classical physics. Rapid advances in nanotechnology are providing access to smaller and smaller devices. What lies at these smaller scales is not just a tiny version of classical information processing, but rather a whole new world of quantum-mechanical information based on coherent quantum dynamics. Specifically, as a consequence of the superposition principle of quantum mechanics, a

"quantum computer" can perform a huge number of computations simultaneously, a phenomenon known as quantum parallelism. Certain problems that are algorithmically "hard" on a classical computer, an example being factorization of large integers into their prime factors, could be solved efficiently on a quantum computer. There are other, possibly equally important applications of quantum computing ranging from the purely scientific, e.g., efficient simulation of quantum systems such as quantum chromodynamics and experimental study of the foundations of quantum mechanics, to the practical, e.g., efficient quantum algorithms for a variety of intractable problems in diverse fields such as network optimization.

Though the theoretical potential of quantum information-processing devices is enormous, implementing the ideas in the laboratory faces serious hurdles. A quantum computation can be implemented using multiple two-level systems called qubits (e.g., atoms or spins) forming a register capable of representing binary numbers. Quantum parallelism stems from the possibility of creating quantum superpositions of many different binary numbers. However, these superpositions are extremely "fragile" and are easily destroyed by coupling to the environment—a process known as decoherence. Furthermore, even in the absence of decoherence, operation of a quantum logic gate requires precision control of the states of the qubits through an external driving field. Our research project targets this crucially important experiment/theory interface.

We have considered two physical systems for implementing quantum information processing: the ion trap (for which experiments are ongoing at Los Alamos National Laboratory) and optical lattices. In an ion trap, positively charged laser-cooled alkali-earth atoms such as calcium are trapped in a combination of electrostatic and radio-frequency fields. The ions interact through their Coulomb repulsion, allowing for quantum logic operations. The ions, however, have a complex internal level structure. Even if highly stable laser fields are resonant with just two levels, the off-resonant excitation of nearby levels can add errors to the operation of the logic gate if not properly accounted for. We have analyzed these effects in a so-called Raman configuration. These results give new insights to experiments at Los Alamos.

In addition to the ion trap, we have explored a new experimental paradigm for quantum computation. Optical lattices are microscopic periodic potentials created by the interference pattern of intersecting laser beams that trap ultracold neutral atoms. When trapped in the wells, atoms can be made to interact by exciting them with external laser beams. This interaction can form the basis of implementing quantum logic gates. The major advantage of this scheme is that unlike the ions, neutral atoms couple very weakly to the environment, and thus decoherence is strongly suppressed. In addition, this system is "scalable" so that it can operate simultaneously on millions of qubits. We have begun to explore the possibilities of this system, and our results appear in *Physical Review Letters.* Moreover, the use of dipole-dipole interactions for quantum logic can be applied in the ion trap as well. We are currently assembling new experiments at Los Alamos to observe such effects for tightly confined yttrium atoms.

Quantum information processing is still in its infancy. Clearly, the optimal physical paradigm has not yet been discovered. Our research pushes the envelope in this direction, giving us deeper insight into the capabilities and limitations of some of the implementations.

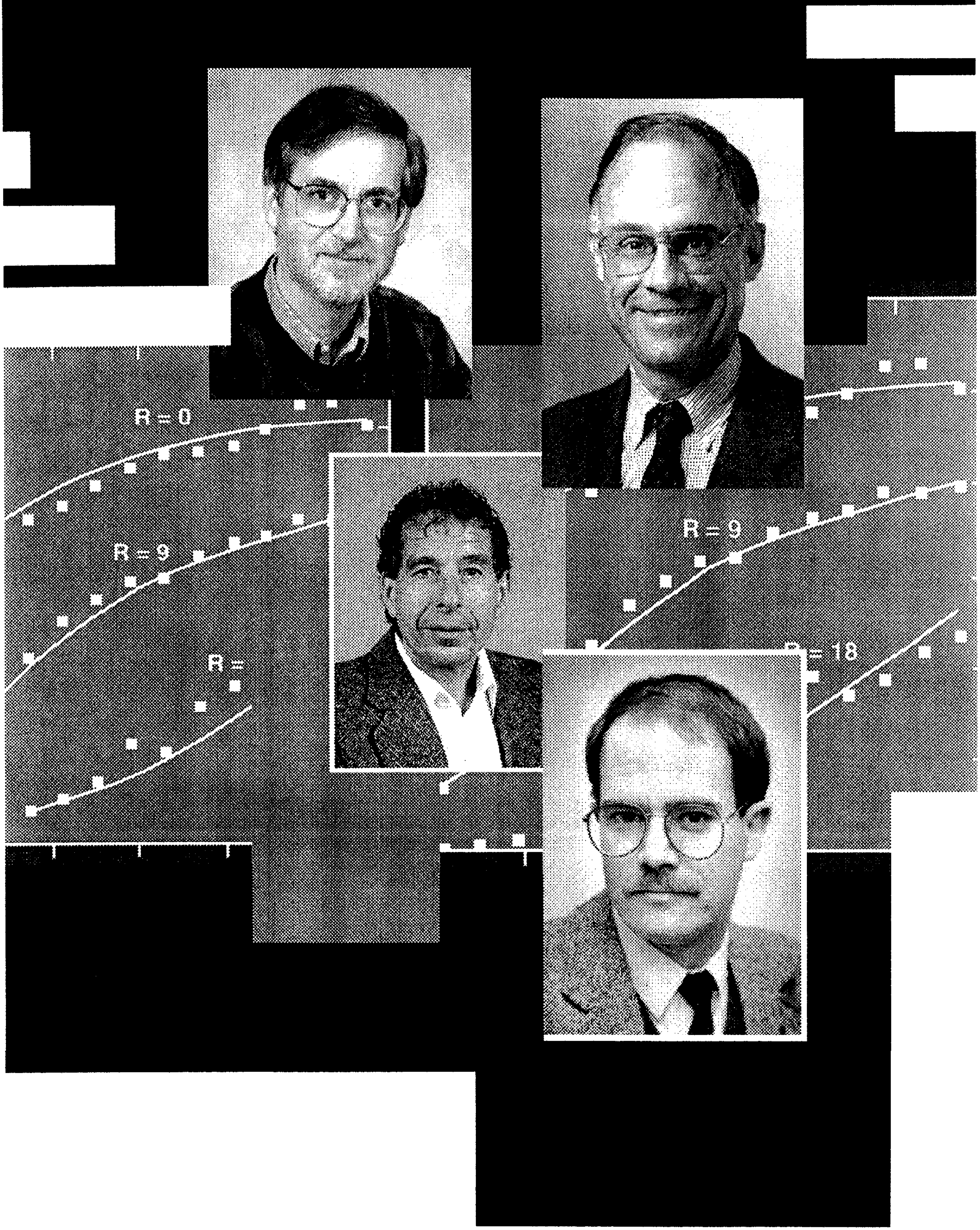
Refereed Publications

Brennen, G.K., C.M. Caves, P.S. Jessen, and I.H. Deutsch, "Quantum Logic Gates in Optical Lattices," *Phys. Rev. Lett.* 82, 1060, (1999).

Presentations

Brennen, G.K., C.M. Caves, I.H. Deutsch, and R.J. Hughes, "Quantum Logic Gates with Neutral Atoms in an Optical Lattice," International Quantum Electronic Conference, San Francisco, CA, May 3–8 1998 (contributed).

Brennen, G.K., C.M. Caves, I.H. Deutsch, and R.J. Hughes, "Quantum Logic Gates with Neutral Atoms in an Optical Lattice," Annual Meeting of the Division of Atomic, Molecular, and Optical Physics of the American Physical Society, Santa Fe, NM, May 3–8 1998 (contributed).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Visiting Scholar Program Progress Reports

The Visiting Scholar Program funds Los Alamos staff members to carry out research and related teaching at UC campuses and UC faulty members to perform research at Los Alamos National Laboratory. The program allows the host institution and the participant to benefit from closer professional interactions while fostering collaborative research between the campus and the Laboratory. The program pays the salary and associated expenses of the participant while he or she czrries out research and related activities at the host institution for a period of between six months and one year. Participants are selected competitively for these appointments by a committee consisting of Vice Chancellors for Research, university faculty members selected by the Academic Senate, and Los Alamos National Laboratory Fellows. Eligibility for the program is limited to UC faculty who are members of the Academic Senate and to Los Alamos technical staff members with regular appointments. Ordinarily, there is an annual call for proposals for the Visiting Scholar Program, with a closing date in February. However, issuing the call depends on the availability of funds. For this reason, there was no call for the FY 1998 and 1999 period. A future call for visiting scholars will be considered as the budget improves, perhaps in 2000.

Since issuing the first call for proposals in August 1995, seven Laboratory-to-campus participants and seven campus-to-Laboratory participants have been selected. Five of these visiting scholars began their appointments between January and September 1996. The other participants began their visits between October 1996 and September 1998. We envision that the Visiting Scholar Program will support an average of four to eight new participants per year, but the number for any period will depend on the availability of funding and candidates.

Five project reports, with listings of personnel, publications, presentations, patents, and awards for FY 1998 follow in this section.

Contents

Final Reports

9852

Research and Instruction in Object-Oriented Computer Code Design and Development for Applications Involving Hydrodynamics in Complex Geometry

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Additional Collaborators: Harry Dwyer and Wolfgang Kollman, Department of Mechanical and Aeronautical Engineering, UC Davis; Joel Keizer, Institute of Theoretical Dynamics, UC Davis

Postdoctoral Fellows: Andrej Bugrim, Institute of Theoretical Dynamics, UC Davis; Thomas Rutaganira, Center for Applied Scientific Computing, Lawrence Livermore National Laboratory

Graduate Students: Tom Kim, Department of Mathematics, UC Davis; Gordana Hofmann-Jovic, Aachen University of Technology, Germany, and UC Davis

Abstract

The method of overset grids is a powerful computational technique for representing complex, often dynamically moving geometry within the context of finite-difference and finite-volume methods for solving partial differential equations (PDEs). A complex region is represented by a number of component computational grids that overlap where they meet and whose union covers the entire domain of interest. This technique has been used successfully to model complex hydrodynamics flows in the fields of aerodynamics, oceanography, combustion, and biology. In this project, the principal investigator (PI) spent six months at UC Davis, where he taught a graduate-level course on overset methods and software, advised graduate students, and interacted with faculty members on various research projects that incorporated the method of overset grids through the Overture software framework, developed at Los Alamos National Laboratory. While at UC Davis, the PI also developed new software modules for handling details of moving complex geometry within the Overture framework. New research projects were begun at the Institute of Theoretical Dynamics, notably two in the area of computational plant and cell biology, which are new fields of application for this software framework. In addition, the PI assisted in beginning the transition of an existing project on aortic blood-flow modeling at UC Davis to the Overture framework. As a result of this successful initial collaboration, the Institute of Theoretical Dynamics has been encouraged by the DOE ER/MICS office to submit a proposal for funding for the purpose of enhancing future interaction and collaboration with members of the Overture project.

Background

The method of overset grids is a powerful technique for representing complex, often dynamically moving geometry within the context of finite-difference and finite-volume methods for solving partial differential equations (PDEs). A complex region is represented by a number of component computational grids that overlap where they meet and whose union covers the entire domain of interest. This technique has been used successfully to model complex hydrodynamics flows in the fields of aerodynamics, oceanography, combustion, and biology. However, it has not enjoyed as widespread use as it might, largely because of the complexity involved in its implementation in computer codes. This complexity arises from the complex data structures that are required for the method and from the difficulty in dealing with those data structures in a general way using conventional procedural programming languages. As a result, its use has been largely confined to the government laboratories and to a few very industrious academic venues.

In work funded by the DOE Office of Science and the DoD Office of Naval Research, the Scientific Computing Group at Los Alamos developed the Overture framework, a set of C++ libraries designed to encapsulate the essential aspects of the overset grid method and provide a user-friendly interface to the technology. The principal investigator (PI) of this project is one of the authors of this software framework. Overture provides a mathematically intuitive interface for writing PDE codes that make use of overlapping grid technology. With this software, it is possible to write simulation codes for some applications in a matter of days, where it once would take months, if not years, to develop a similar capability.

Progress

While at UC Davis, the PI taught a graduate-level course titled "Numerical Techniques for Solving Partial Differential Equations in Regions of Complex Geometry." The course met twice a week during the winter quarter; approximately ten students, postdoctoral fellows, and faculty members attended on a regular basis. The course covered basic theory of numerical methods for PDEs and included homework assignments in which students wrote computer codes using the Overture framework, demonstrating the basic concepts being taught. The course and course notes were the basis for three projects that began during that time, in which the framework was used to perform numerical studies for various scientific purposes. Significantly, in the case of Csutora et al. (1999) and Kim et al. (1999), these studies represent the use of computational simulations for problems that have previously been deemed intractable. Researchers in those fields typically lack the computational sophistication to perform simulations that involve nontrivial and, in the case of Kim et al. (1999), moving geometry. The high-level interface provided by the Overture framework for solving PDEs in complex geometry allowed these researchers to write the computer codes and perform these simulations relatively painlessly. In the case of Hoffman-Jovic (1998), the publication describes a computational project that contributes to the student's engineering degree at RTWH-Aachen in Germany.

Since returning from UC Davis, the PI has initiated a new collaborative effort with researchers at the Institute of Theoretical Dynamics to study mammalian aortic cardiovascular flow. In this project, a postdoctoral fellow with the Overture project, now located at the Center for Applied Scientific Computing at Lawrence Livermore National Laboratory is working half of his time at Lawrence Livermore and half at UC Davis. The PI's visit was also responsible for the decision by a campus collaborator to change his overset-grid-based research efforts in computational combustion and computational biology to include use of the Overture framework. This decision was based in large part on the flexible grid-generation capabilities available in Overture and on the high-level programming environment provided, since both of these capabilities reduce the learning curve for new graduate students and postdoctoral fellows on that research project. In addition, as a result of the PI's successful UCDRD-funded visit to UC Davis last year, several campus collaborators have been encouraged by the DOE Office of Science Mathematics and Computational Science department to submit a proposal for funding to continue collaborations in the areas of mathematical biology and computational combustion.

Refereed Publications

Csutora, P., H.Y. Kim, A. Bugrim, K.W. Cunningham, R. Nuccitelli, J.E. Keizer, M.R. Hanley, and R.B. Marchase, "Calcium Influx Factor is

Synthesized by Yeast and Mammalian Cells Depleted of Organellar Calcium," *PNAS* 96, 121 (1999).

Kim, T.K., W.K. Silk, and A.Y. Cheer, "A Mathematical Model for pH Patterns in the Rhizosphere of Growth Zones" (submitted to *Plant, Cell and Environment*) (1999).

Unrefereed Publications

Brown, D.L., "Moving Grid Classes for Overture, User Guide and Reference" (to be published as a technical report by Lawrence Livermore National Laboratory (1999).

Hoffman-Jovic, G., "Navier-Stokes Solver for the Incompressible Navier-Stokes Equations, Written Using Overture, an Advanced Object-Oriented Software System for Solving PDEs," Studien-arbeit, RTWH-Aachen, Germany (1998).

Presentations

Brown, D.L., and W.D. Henshaw, "OVERTURE: Object-Oriented Tools for Solving CFD and Combustion Problems," 1998 Advanced Simulation Technologies Conference, Boston, MA, April 5–9, 1998 (contributed).

Bugrim, A., J. Keizer, R. Fontanilla, and R. Nuccitelli, "Initiation Mechanism of the Fertilization Ca^{2+} Wave in Xenopus Eggs," Pacific Symposium on Biocomputing, Hawaii, 1999 (contributed).

Keizer, J., A. Bugrim, R. Fontanilla, and R. Nuccitelli, "Quantitative Studies of the Fertilization Ca^{2+} Wave in Xenopus laevis Eggs," Meeting of the American Society for Cell Biology, San Francisco, CA, 1998 (contributed).

Wagner, J., A. Bugrim, J. Keizer, R. Fontanilla, and R. Nuccitelli, "Quantitative Studies of the Fertilization Ca^{2+} Wave Initiation Mechanism in Xenopus laevis Eggs," Meeting of the Biophysical Society, Baltimore, MD, 1999 (contributed).

9856
Muon Spin Rotation in Strongly Correlated Electron Systems

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Abstract

Electronic structure, magnetism, and superconductivity in highly correlated electron materials (Kondo/heavy-fermion systems and colossal magnetoresistance manganese oxides) have been investigated by using nuclear magnetic resonance, muon spin rotation (μSR), and x-ray-absorption fine-structure (XAFS) techniques. Evidence has emerged from these experiments that sample inhomogeneity, either spontaneous or associated with structural disorder, is crucial to the behavior of these systems. In particular, non-Fermi-liquid (NFL) behavior in heavy-fermion alloys can in some cases be due to an inhomogeneous distribution of Kondo temperatures T_K arising from disorder in the random alloy. Such "Kondo disorder" modifies and in some cases competes with critical-fluctuation-based mechanisms for NFL behavior that have been proposed theoretically assuming a homogeneous system. XAFS measurements of the local structure in the nominally ordered NFL compound UCu_4Pd indicate a lattice-disorder origin for NFL behavior in this material. Zero-field μSR experiments on the Kondo compound $PrInAg_2$ (where there is no reason to suspect inhomogeneity) rule out a magnetic origin (spin freezing or a conventional Kondo effect) for the previously observed specific heat anomaly at ~0.5 K and confirm the attribution of this anomaly to an unconventional nonmagnetic Kondo effect. Muon spin rotation and resistivity experiments on the colossal magnetoresistance (CMR) manganites $La_{0.67}Ca_{0.33}MnO_3$ and $La_{1.4}Sr_{1.6}Mn_2O_7$ probe inhomogeneous spin and charge structures (magnetoelastic polarons) which are believed to be intimately associated with the CMR phenomenon.

Background

The Visiting Scholar appointment of D. E. MacLaughlin for residence at Los Alamos from September 1997 to August 1998 was for the purpose of carrying out experimental studies of a number of problems in the physics of highly correlated electron materials using the muon spin rotation (μSR) technique. Our experiments study systems with potential relations to interesting technological applications, such as high-temperature superconductivity and colossal magnetoresistance (CMR).

Projects were selected in three areas of considerable current interest.

- Unusual non-Fermi liquid (NFL) behavior in several *f*-electron-based heavy-fermion compounds and alloys, which was also studied using nuclear magnetic resonance (NMR). In heavy-fermion metals conduction electrons interact with the spins of localized (*f*-ion) atomic magnetic moments, which are screened to form a complicated many-body singlet or near-singlet Kondo ground state. The canonical picture of this state is furnished by Landau's Fermi-liquid theory, in which interactions between electrons do not modify the essential behavior of low-lying excitations unless a phase transition occurs. Probes of these excitations such as specific heat and magnetic susceptibility give unambiguous evidence that on the contrary the low-lying excitations are much more numerous than expected—thus the term "NFL behavior." This phenomenon may be related to effects seen in the high-T_c copper oxides.

- An unconventional nonmagnetic Kondo effect in the praseodymium-based heavy-fermion compound $PrInAg_2$. Here the $(2J+1)$-fold degenerate ground-state multiplet of the Pr^{3+} *f*-ion can be split by electric fields within the crystal, resulting in a degenerate but nonmagnetic ground state. This nonmagnetic object can in turn screen its charge (not spin) degrees of freedom via the so-called "quadrupolar Kondo effect" (QKE), analogous to the spin Kondo effect described above. The QKE has been predicted theoretically, but never observed until a recent specific-heat study of $PrInAg_2$ gave indirect and somewhat controversial evidence for a QKE below 1 K in this compound.

- Studies of spin dynamics in manganese oxides that exhibit CMR. Such materials may have applications such as nanoscale read heads for magnetic data storage devices. Charge, spin, and lattice degrees of freedom are strongly coupled to each other in these systems, and local probes such as μSR are invaluable in determining behavior on the atomic scale.

In the μSR technique spin-polarized muons, obtained from a so-called "meson factory" accelerator (examples are TRIUMF in Vancouver and the Paul Sherrer Institute, or PSI, in Zurich), are implanted in the sample. The direction of emission of the subsequent decay positron, which is related to the muon spin orientation at the time of decay, is monitored with standard techniques of experimental nuclear physics. In the majority of experiments, positive muons are used, which can be considered short-lived impurities after they come to rest at interstitial sites in the sample.

Magnetic resonance (μSR and NMR) provides microscopic information on the structure of solids via determination of static and dynamic properties of local magnetic fields at spin-probe sites. The paramagnetic resonance shift in an applied magnetic field (Knight shift in a metal) is a measure of the local spin susceptibility. Resonance line shapes are often determined by distributions of local fields. These parameters are extremely sensitive to changes of charge and spin distributions with experimental conditions, in ways that will be discussed below in more detail.

The experimental details of μSR and NMR are very different, but the results are analyzed in similar ways and yield similar information. Important intrinsic differences between them motivate the application of both techniques to certain problems. Both μSR and NMR techniques are strong points of the research program of the Condensed Matter and Thermal Physics Group at Los Alamos.

MacLaughlin has a long history of collaboration with μSR and NMR research at Los Alamos, dating from 1978. One of his recent Ph.D. graduate students carried out NMR dissertation research at Los Alamos with funding by the UC/Los Alamos collaborative INCOR program. In recent years our μSR effort has broadened into large collaborative programs with a number of other groups at accelerator facilities at PSI in Zurich and TRIUMF in Vancouver. Our co-workers are from research groups at universities (UC San Diego, Columbia University, Florida State University, and University of Florida), government laboratories (Los Alamos and Ames Laboratory), and industrial laboratories (Lucent Technologies Bell Labs). We also have ongoing collaborations with research groups abroad (Leiden University, ETH Zurich, and PSI).

UC Riverside and Los Alamos share responsibility for coordination of the research described above, which entered a critical phase last year. Work during MacLaughlin's visit concentrated on acquiring and characterizing samples, carrying out experiments during extensive experimental periods at PSI and TRIUMF, and analyzing the data. His travel to TRIUMF and PSI, as well as other costs related to this research, was funded by a continuing research grant from the National Science Foundation during the past year; future travel will be financed in part through a no-cost extension to the Visiting Scholar funding. Much of the research effort consisted of working with collaborators who are carrying out their own research on the systems used for the μSR experiments. This allowed us to make optimum use of what is already known about the materials of interest and to ensure that the samples studied yielded the maximum amount of information. Many of these collaborators were at Los Alamos. MacLaughlin's visit led to a dedicated period of interaction with these people, some of whom brought a keen interest to the NFL, μSR, and NMR work described above.

Progress

Muon spin rotation experiments on a stoichio-metric sample of UCu_4Pd, in which recent neutron-scattering experiments suggest an ordered structure, indicate that the uranium-ion susceptibility is strongly inhomogeneous at low temperatures. We argue that this is due to residual disorder, which also dominates NFL behavior. The data yield a short correlation length (<1 lattice spacing) and a rapid, low-temperature uranium-moment relaxation rate ($>10^{12}$ s^{-1}), which constrain cluster-based models of NFL behavior.

X-ray-absorption fine-structure (XAFS) measurements of the local structure in UCu_4Pd, carried out at Los Alamos, indicate a probable lattice-disorder origin for NFL behavior in this material. A distribution of palladium-copper distances was observed, consistent with 24 ± 3% of the palladium atoms occupying nominally copper sites. A Kondo disorder model, based on the effect on the local Kondo temperature T_K of this interchange and additional bond-length disorder, qualitatively reproduces the empirical distribution $P(T_K)$ obtained from magnetic resonance experiments and agrees with experimental susceptibility and specific heat data.

Muon spin relaxation experiments have also been carried out in the Kondo compound $PrInAg_2$. The zero-field muon relaxation rate was found to be independent of temperature between 0.1 and 10 K, which rules out a magnetic origin (spin freezing or a conventional Kondo effect) for the specific heat anomaly observed at ~0.5 K. The low-temperature muon relaxation is quantitatively consistent with nuclear magnetism including hyperfine enhancement of the ^{141}Pr nuclear moment. This is strong evidence (1) against a Pr^{3+} electronic magnetic moment and (2) for the G_3 crystalline-electric-field-split ground state required for a non-magnetic route to heavy-electron behavior. The data imply the existence of an exchange interaction between neighboring Pr^{3+} ions of about 0.2 K in temperature units, which should be taken into account in a complete theory of a nonmagnetic Kondo effect in $PrInAg_2$.

Silicon-29 NMR linewidths in the heavy-fermion alloy $CeRhRuSi_2$ increase rapidly with decreasing temperature and reach large values at low temperatures, indicative of a broad distribution of local magnetic susceptibilities. For temperatures above 1 K, the magnitude and temperature dependence of the linewidth is in good agreement with disorder-driven theories of NFL behavior that invoke wide distributions of local susceptibilities χ_j. In particular, the NMR linewidths agree well with a distribution function $P(\chi)$ which fits specific heat and susceptibility data. The return to Fermi-liquid (FL) behavior observed below 1 K is manifested in the vanishing of $P(\chi)$ as $\chi \rightarrow \infty$, indicating the absence of strong magnetic response at low energies. Our experimental results point out the need for an extension of current theories of disorder-driven NFL behavior in order to incorporate this low-temperature crossover.

Zero-field μSR experiments on the colossal magnetoresistance (CMR) manganite $La_{0.67}Ca_{0.33}MnO_3$ powder show that for $T \leq T_C$ the spontaneous muon frequency $\nu_\mu(T)$, which is proportional to the sublattice magnetization, is well described by $(1-T/T_C)^\beta$, where $\beta = 0.345 \pm 0.015$, characteristic of a second-order phase transition for a three-dimensional (3-D) spin system. The ferromagnetic transition temperature ($T_C = 274$ K) and resistivity peak temperature coincide to within 1 K. Below T_C, $\nu_\mu(T)$ and the zero-field resistivity ρ are correlated, with $\nu_\mu(T) \propto -\ln \rho$. Unusual relaxational dynamics suggest spatially inhomogeneous manganese-ion correlation times. These results have been interpreted in terms of the possible effects of polarons on the spin and charge dynamics.

We have also carried out zero-field muon spin rotation experiments in single crystals of the anisotropic bilayer CMR system $La_{1.4}Sr_{1.6}Mn_2O_7$ for $T = 5$–325 K. The spin-lattice relaxation rate is spatially inhomogeneous below the 3-D magnetic transition temperature T_C and anisotropic above T_C. We find evidence against two-dimensional spin ordering and in favor of isotropic spin fluctuations above T_C. In addition, the very slow spin fluctuations found below T_C in cubic (3-D) perovskites like $(La,Ca)MnO_3$ or $(La,Sr)MnO_3$ and attributed to relatively small magnetoelastic polarons, are absent in $La_{1.4}Sr_{1.6}Mn_2O_7$. This suggests that at a given reduced temperature relative to T_C, the polaron size in the layered material is significantly larger than in the 3-D perovskites.

Refereed Publications

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Nachumi, B., Y. Fudamoto, A. Keren, K.M. Kojima, M. Larkin, G.M. Luke, J. Merrin, O. Tchernyshyov, Y.J. Uemura, N. Ichikawa, M. Goto, H. Takagi, S. Uchida, M.K. Crawford, E.M. McCarron, D.E. MacLaughlin, and R.H. Heffner, "Muon Spin Relaxation Study of the Stripe Phase Order in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ and Related 214 Cuprates," *Phys. Rev. B* 58, 8760 (1998).

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Presentation

MacLaughlin, D.E., "Kondo Disorder and Non-Fermi-Liquid Behavior in Heavy-Fermion Systems", Condensed Matter Seminar, Physics Department, University of Florida, October 1997 (invited).

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Plasma Modeling at the UCLA Plasma Physics Laboratory

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Abstract

The purpose of the current research is to apply the Los Alamos suite of atomic physics and plasma kinetics codes to study the population dynamics of several plasmas being studied at UC Los Angeles. One project involves studying the plasma formation in the large plasma device (LAPD) at UC Los Angeles. The LAPD uses an electrical discharge in a chamber filled with inert gas to create conditions that are similar to those occurring in space. Measurements of electron density, temperature, and line emission have been compared to detailed computer simulations using the Los Alamos codes. The results provide a detailed understanding of LAPD plasma formation. For most of the duration of the discharge, the

plasma charge-state distribution is far from equilibrium and underionized for the temperatures that are typically observed. Time-dependent calculations, using the measured electron temperatures during the course of the discharge, reproduce very well the observed electron density profiles at several spatial positions in the device. Here, thermal Maxwellian electron distributions are sufficient to explain the observed results. However, nonthermal electrons probably account for the very high ionization rates that are observed very early in the discharge. More calculations and experiments, including spectroscopic measurements, are required to obtain a full understanding of the kinetics occurring in the LAPD. The study has also identified some possible areas of improvement for the Los Alamos codes, including a more extensive treatment of nonthermal electrons.

Another area of research involves the plasma occurring in the sodium and calcium layers of the ionosphere. This plasma is of interest for applications in light detection and ranging and for the creation of artificial guide stars. Models were calculated for both sodium and calcium that can be used to provide a temperature diagnostic for atmospheric plasmas heated by an external source, for example, from a ground-based transmitter. Calculations with the Los Alamos codes predict enhanced emission from various spectral lines, which would not emit under ambient temperatures, and thus providing a diagnostic of plasma heating.

Radiative power loss calculations for hydrogen, helium, and oxygen were also performed during the visiting scholar appointment. Such data is important for studying the effect of impurities on the performance of magnetic fusion devices, like the tokomak reactor that is currently under construction at UC Los Angeles. Here, even small amounts of impurities, for example, oxygen from water or air, can radiate away significant amounts of energy and degrade fusion efficiency. Atomic models were calculated for hydrogen, helium, and oxygen; these were used in time-dependent and steady-state kinetics calculations to predict the total radiation output from these elements under various conditions. Preliminary calculations show that a 1% oxygen impurity can increase the radiation output of a pure hydrogen plasma by over 3 orders of magnitude. It is hoped that these results can be compared quantitatively to future experiments.

Background

The large plasma research device (LAPD)[1] at UC Los Angeles is a large, linear research device designed primarily for studying fundamental processes in space plasmas. The LAPD has an oxide-coated cathode that produces a 10-meter-long plasma column in a large vacuum chamber. The machine is surrounded by 68 coils, which produce an axial magnetic field of up to 3000 G. Helium and argon are usually used as the fill gases. The machine is designed to have a 1-Hz repetition rate for ample data acquisition. In addition, 128 radial ports are provided for diagnostic purposes. The machine has been scheduled for upgrading in the near future.

Traditionally, the machine has been used to perform plasma physics experiments by launching various types of waves into the formed plasma. More recently, laser-induced fluorescence has been used to determine the widths of various spectral lines. The plasma ion temperature may be deduced from the line widths that are due to Doppler broadening. Thus, the current interest in spectral line formation has led to a desire to understand the overall population dynamics and the charge-state distributions in the LAPD.

The Los Alamos atomic physics and plasma kinetics codes provide computer models that can be used to simulate level populations in various plasma sources. The atomic physics codes provide energy levels and cross sections for excitation and ionization by both electrons and photons. The cross sections are used to calculate rate coefficients based on the plasma environment through the electron energy distribution and the radiation field. Level populations are obtained from the solution of rate equations. The spectral properties are then derived from the calculated level populations and radiation rates.

The simulations of the LAPD plasma will represent a challenge for the Los Alamos codes. First, the electron temperatures encountered in the LAPD are lower than those normally considered, and neutrals play an important role. The electron energy distribution in the LAPD is non-Maxwellian and consists of a high-energy component of primary electrons and a low-energy component of secondary electrons. The primary electrons have energies near 50 eV and correspond to the applied current. The secondary electrons are mainly thermal (6 to 10 eV) and result from the ionizing collisions of primary electrons with the fill gas. Energy transfer from primary electrons to secondary electrons is also important for maintaining the relatively high temperature of the secondary electrons. This is evident because the plasma temperature drops significantly when the discharge is complete. Calculations show that the level populations occurring in the LAPD are highly transient, time evolving, and non–steady state. The current is applied for only a few milliseconds, whereas the equilibration times are of the order of tenths of seconds for typical LAPD plasma densities. Therefore, the plasma is underionized compared with steady-state conditions for similar temperatures.

Another challenge involves the simulation of lines in the visible spectrum. Even though much of the radiation emitted by the LAPD is in the ultraviolet, the lines used for diagnostics occur in the visible spectrum. This is mostly due to the unavailability of instrumentation for detecting ultraviolet radiation. The visible spectral lines are the result of transitions between excited states of high principal quantum number. Hence, the modeling of high-lying levels is required, and enough detail must be included in the simulations in order to accurately represent these states.

Progress

An experiment was performed to measure electron density and temperature during the discharge. For this experiment, the 40-cm-diameter oxide-coated cathode produced a 2.95-kA discharge current with a discharge voltage near 50 V. The duration of the discharge pulse was about 3 ms, and the repetition rate was 1 Hz. The chamber was filled with helium at a pressure of 1.1×10^{-4} torr, which corresponds to a gas density of 2.6×10^{12} cm^{-3}. For confinement, a uniform axial magnetic field B_0 of 1200 G was generated by solenoidal magnet coils around the machine.

The electron density and temperature were measured at various times during the discharge by using a Langmuir probe and microwave interferometry. The probe measurements alone do not yield absolute values for plasma density because the background magnetic field constrains the magnitude of the current collected by the probe. To compensate, a microwave interferometer is used to measure the line-integrated phase shift across the diameter of the plasma, which is directly related to the line integral of the plasma density profile. Then 50 to 60 Langmuir probe measurements across the diameter of the plasma are taken, which yield a radial plasma density profile of relative magnitude. By numerically integrating the measured density profile and scaling it to produce a computed phase shift equal to the measured phase shift, we effectively calibrate our Langmuir probe density measurements for a given magnetic field and range of plasma parameters.

A detailed atomic model for helium was calculated using the Los Alamos suite of atomic physics codes. The model includes each individual fine structure level designated by the usual ${}^{2S+1}L_J$ quantum numbers for all configurations of the type $1s^2$, $1snl$, $2snl$, and $2pnl$ in neutral helium and nl in ionized helium. All valid combinations of principle quantum number n and orbital angular momentum l through $n=10$ and $l=9$ were considered. Oscillator strengths for all dipole-allowed transitions were also calculated. Therefore, all the singlet and triplet states in neutral helium through $n=10$ are included individually, and their associated optical transitions are resolved. In addition, a set of electron impact-excitation, electron impact-ionization, and photoionization cross sections were calculated. First-order many-body (FOMBT) collision strengths were calculated for the $1s^2$-$1snl$, $1s2s$-$1snl$ and $1s2p$-$1snl$ transitions in neutral helium. For ionized helium, FOMBT was used for the $1s$-nl, $2s$-nl, and $2p$-nl transitions. Plane-wave Born cross sections were used to fill in the remaining transitions. Therefore, both ground-to-excited and excited-to-excited transitions are considered. Electron impact-ionization cross sections were calculated using the distorted wave method from the $1s^2$, $1s2s$, and $1s2p$ levels of neutral helium. By comparison with distorted wave calculations, scaled hydrogenic cross sections were found to be sufficiently accurate for ionization out of other levels. Photoionization cross sections from all levels in each ion stage were calculated using the distorted continuum functions. Autoionization rates for the doubly excited states of neutral helium were also calculated for the inclusion of autoionization and dielectronic capture.

The level populations and free-electron density are calculated by solving the rate equations as a function of time. The equations involve a rate matrix that contains net rates for all processes that can transfer population between levels. These net rates are expressed in terms of rate coefficients for each individual process evaluated for the given plasma conditions. The equation for the free-electron density is expressed in terms of rate coefficients for all processes that produce or recombine free electrons. The rate coefficients for processes involving electron collisions are calculated by integrating the calculated cross sections over a Maxwellian energy distribution. Elements of the rate matrices also include multiplicative factors of the electron density for processes induced by electron collisions. The equations are solved, given a set of initial conditions. The processes included are collisional excitation and deexcitation, spontaneous radiative decay, collisional ionization, three-body recombination, radiative recombination, autoionization, and dielectronic capture.
The plasma is assumed to be optically thin, thus any photons that are produced are lost without further altering the kinetics. Processes involving doubly excited states were found to be of little consequence for the plasma conditions under consideration and were subsequently discarded in the simulations to avoid unnecessary computation. A system of approximately 300 coupled differential equations was solved for this study.

Figure 1 shows a comparison of experiment and calculation for radial positions of 0, 9, and 18 cm from the center of the plasma column. The boxes shown in the figure correspond to the measured values of electron density for various times in the discharge; the solid lines correspond to the numerical integration of the rate equations discussed above. The starting point for the integration was the earliest measured time point for the cases in which $R = 0$ and $R = 9$. The initial population density of He^+ was taken to be the measured electron density at that point, assuming that the He^{++} population density is negligible. The total density, neutrals plus ions, was fixed at the measured value of 2.6×10^{12} cm^{-3} for the integration.
The measured temperatures at the succeeding time points which range from approximately 6 to 8 eV were then used in the rate equations to propagate the electron density to later times, which is shown by solid lines in the figure. The variation in electron density with radial position, apparent in the figure, is most likely caused by the discharge current spreading radially with time. Initially, the

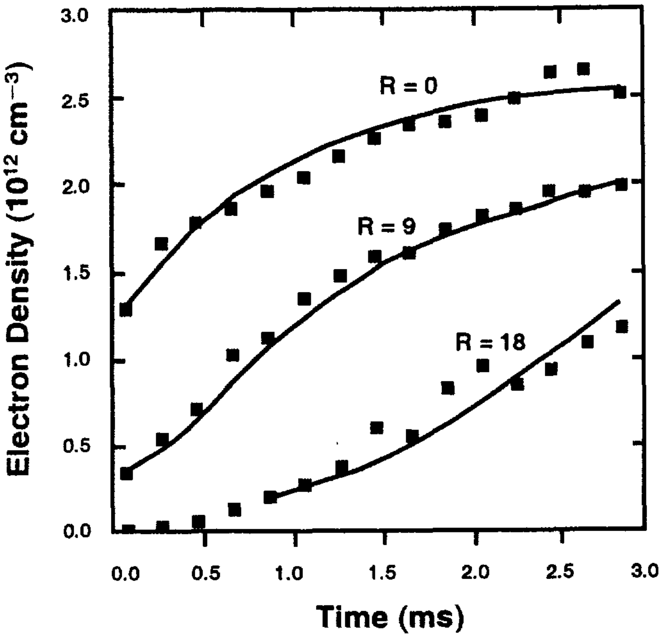

Fig. 1. Comparison of experiment and calculation.

ionization rate is most rapid near R=0 and slower at larger radial positions in the column. The starting point for the R=18 calculation was taken at a somewhat later time, 0.8 ms. In this case, the electron density is not well developed at early times, and the effects of the nonthermal discharge electrons are significant.

An integration from an earlier time point yields a density curve that underestimates the ionization, consistent with the model used here, which is based on Maxwellian electron energy distributions, and does not account for the action of the faster discharge electrons. Hence, the concept of electron temperature at early times and low electron density is ambiguous. However, once enough thermal electrons are produced, a reasonably good starting point is established, and the calculation is in agreement with the experiment.

A paper describing the work discussed above is to be published by the *Journal of Physics B*. The authors are not aware of any other similar calculations for these conditions and refer readers to the manuscript for more details. The authors also feel that a continued collaboration between UC Los Angeles and Los Alamos would be highly desirable and beneficial to both institutions.

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Refereed Publication

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R.E.H. Clark, "Time Dependent Kinetics
Model for a Helium Discharge Plasma"
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Long-Term Issues for Nuclear Stewardship and Fissile-Material Disposition

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Abstract

Nuclear stewardship requires detailed, quantitative assessment of stocks and flows of fissile and radioactive materials resulting from civilian power production and nuclear weapons programs, under a variety of power and weapons stockpile scenarios, to provide quantitative predictions of potential long-term consequences of current policy options. The one-year sabbatical discussed here, completed in July 1998, focused on the broad topic of long-term outcomes from fuel cycle and weapons material disposition options using direct disposal of spent fuel and immobilized plutonium in geologic repositories.

The work focused on two topics that have received relatively less attention than potential environmental releases from repositories: (a) the potential for accumulation of critical configurations of fissile material and the subsequent response and (b) safeguards and security issues for geologic repositories. The work benefited from the unique expertise and resources that exist at Los Alamos National Laboratory for studies in these areas. The primary efforts of the sabbatical focused on quantifying seismic emission from alternative tunneling technologies and evaluating the implications for implementing long-term safeguards for repositories containing spent fuel and excess weapons plutonium, and on applying unique Los Alamos code capabilities to modeling the dynamic response of autocatalytic underground deposits of fissile material. The most important result of the study on long-term repository safeguards was to note that some excavation methods for small-diameter tunnels could potentially escape detection and that significant reduction in the long-term proliferation attractiveness of repositories may come from reprocessing. For the study of autocatalytic response of fissile material deposits in repositories, it was found that large deposits could generate substantial energy releases but that with nonuniform deposition criticality is likely to occur first in small regions with only modest energy release.

Background

Nuclear stewardship requires detailed, quantitative assessment of stocks and flows of fissile and radioactive materials resulting from civilian power production and nuclear weapons programs, under a variety of power and weapons stockpile scenarios, to provide quantitative predictions of potential long-term consequences of current policy options. The one-year sabbatical discussed here, completed in July 1998, focused on the broad topic of long-term outcomes from fuel cycle and weapons material disposition options using direct disposal of spent fuel and immobilized plutonium in geologic repositories. The work focused on two topics that have received relatively less attention than potential environmental releases from repositories: (a) the potential for accumulation of critical configurations of fissile material and the subsequent response and (b) safeguards and security issues for geologic repositories. The work benefited from the unique expertise and resources that exist at Los Alamos National Laboratory for studies in these areas. The specific studies and tasks completed during the one-year sabbatical at Los Alamos are outlined below.

Long-Term Safeguards and Security for Fissile Material in Geologic Repositories

Current plans in the United States and Sweden, and lack of plans in many other countries, make it possible that commercial spent fuel may be disposed of in multiple geologic repositories. In addition, excess weapons plutonium and plutonium in waste will be removed from DOE inventories in the United States for disposal. Disposal decisions made in the next few decades will provide the long-term boundary conditions for nuclear nonproliferation efforts. In parallel with work to predict and minimize long-term environmental releases of radionuclides from such repositories, additional investigation is being focused to predict and minimize long-term proliferation risks from such repositories. Such repositories may provide attractive sources of fissile material compared to the traditional approach using dedicated production facilities, in particular because plutonium production rates can be high.

Per F. Peterson's interest in the repository safeguards question has been motivated primarily because this topic will require research in the future, now that the International Atomic Energy Agency has specifically stated that it will require long-term safeguards on repositories for spent fuel. Monitoring for acoustic emission from tunneling machinery, periodic satellite surveillance, and site visits are the primary methods proposed for detecting undeclared excavation. Of these, only acoustic monitoring can detect subsurface activity, allowing a fixed monitoring perimeter to be established around a repository. If acoustic monitoring can be defeated and if other subsurface detection methods are unavailable, then surface monitoring must be performed for a larger, more ambiguous radius around the repository. This research created a fundamental classification scheme for identifying excavation technologies. The classification allows definition of a spectrum of small-diameter tunnel excavation scenarios. Analysis suggested that even for hard rock, national groups may be able to field compact, modular hydraulic or thermal excavation machinery with acoustic emission below background noise levels, as illustrated in Fig. 1.

The analysis to be published as a result of this research supports the following observations:

- A group attempting undeclared excavation into a spent-fuel repository would select a small tunnel size, likely under 2 m high, much different from the tunnels excavated for the original repository construction.
- A clandestine tunneling group would select compact, modular excavation machinery. The tunnel entrance could be hidden by a small, unremarkable structure.
- On the basis of the limited data available in the literature, a scenario for hydraulic excavation of granite with water jets can be constructed that keeps acoustic emission at background seismic noise levels at distances of tens of meters, for a 10 m/day advance rate. With additional development, a national group could potentially field thermal or hydraulic excavation machinery that would be undetectable by passive acoustic methods at a few tens of meters or less.
- A variety of human surface activities, such as light industry and construction of residences and farm and ranch structures, could conceal surface

observation of a clandestine tunneling attempt using compact, modular equipment, unless subjected to sufficiently rigorous on-site monitoring.

- The resistance of soft rock (clay shale and salt) to clandestine tunneling will be much lower than the resistance of hard rock. Penetration rates can be substantially higher in soft rock, and acoustic and thermal emission can be orders of magnitude lower. Theft by subnational groups is much more readily conceivable for soft-rock repositories.

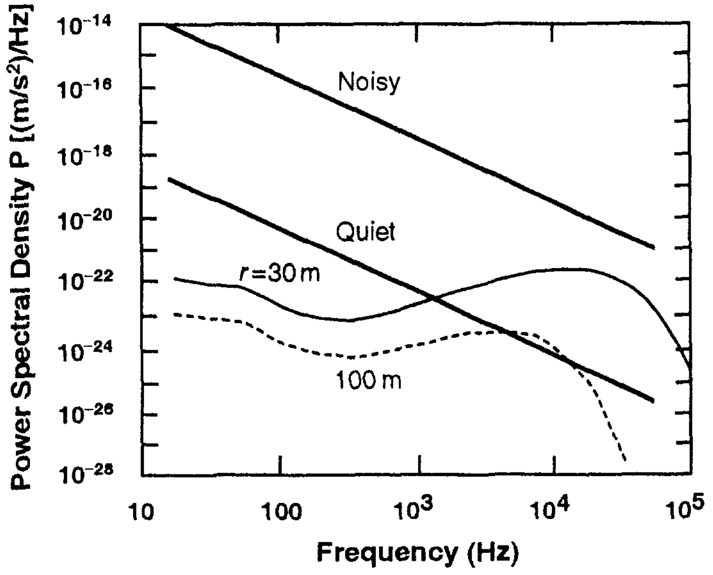


Fig. 1. Power spectral density in low-attenuation granite due to reference water jet impact with a force totaling 10,000 N and power spectrum measured experimentally for a typical high-pressure water jet, at radii of 30 m and 100 m from the tunnel face. Shown for comparison are typical power spectra of ambient seismic noise for hard basement rock.

If subsurface monitoring by acoustic or other geophysical methods proves to be unreliable, this has a significant negative implication for the viability of repository safeguards because the area that must be covered by surface monitoring grows substantially. This suggests that additional engineering design and experiments are warranted to study the feasibility of detecting hydraulic and thermal excavation methods. These studies should focus on the detection of small-diameter tunnels, rather than the larger diameters that would be used originally to emplace waste.

On the basis of the analysis presented here, future repository monitoring and safeguards burdens could be reduced in four ways:

- Select hard-rock sites (granite or welded tuff) with minimal vegetation and no nearby bodies of water to maximize the technical difficulty of undeclared tunneling.

- Select sites where future surface activities would have low economic potential (i.e., desolate sites), and consider requirements that the host nation agree to permanently prohibit human activities involving the construction of any surface or subsurface structures, except structures directly required for repository construction and operation, for a suitable radius around the site (i.e., perhaps 15 km). Make provisions for unrestricted on-site inspections to a significantly larger radius (i.e., perhaps 40 km), to deter long-term, long-distance attempts to construct tunnels.

- Minimize the number of repository sites by forming multinational high-level waste compacts. Although most nations could conceivably identify repository sites inside their borders that would protect future human health and safety, many do not have areas that meet the first two safeguards criteria. Forming international compacts for waste disposal would also help minimize the number of repositories that future generations would be required to monitor. Waste trading could allow the disposal of waste of lower attractiveness at repository sites with weaker proliferation resistance. Potential choices for repository host nations for attractive waste forms would be the United States, Russia, and China.

- Study and develop waste treatment processes that would reduce substantially the concentrations of weapons-usable isotopes in repository waste forms, to increase the mass of material that must be recovered to obtain a given quantity of fissile material, as well as the magnitude and duration of the radiation barrier protecting the material.

These siting criteria have the potential to reduce the long-term burden that repository safeguards will place on future generations. The prohibition of all surface and subsurface structures that could conceal even a small tunnel entrance would make the construction of any structures, which could be readily detected by periodic satellite observation, a clear violation of the host nation's safeguards agreement. Reducing the concentrations of weapons-usable isotopes in waste forms, even if just for a subset of the world's repositories, could reduce the attractiveness of undeclared excavation and help deter such efforts. Alternative disposal methods, such as seabed or ocean-island disposal, can also be reconsidered as providing greater barriers to undeclared recovery.

Of repository sites currently under consideration in various nations, the Yucca Mountain site in the United States most readily meets the safeguards criteria of hard rock (welded tuff) and low economic potential. The sparsely vegetated, sparsely populated site is located on federally managed land overlapping the Nevada Test Site, Nellis Air Force, and Bureau of Land Management (BLM) lands. The closest farm lands are 25 km away, in the Amargosa Desert and Oasis Valley. Grazing occurs on leased BLM land 10 km away. Highway 95 from Las Vegas passes within 20 km of the proposed repository; the closest towns are Amargosa Valley (22 km) and Beatty (30 km). Active surface and underground mining occurs at Bare Valley (20 km), and mining has occurred previously at other locations, the closest being Amargosa Desert (18 km) and Lee (22 km). The Desert National Wildlife Range occupies a large area to the east of the site.

Although the Yucca Mountain site provides hard rock in a federally owned area of low economic potential, legislative action would be required to increase the current limits on the maximum mass of spent fuel that can be stored at this site, just to accept the spent fuel that existing U.S. plants will generate over their current operating licenses. Recommendations to also accept commercial spent fuel from other countries to achieve long-term nonproliferation goals would likely encounter strong domestic opposition.

Reprocessing, with several caveats, has the potential to significantly reduce the long-term attractiveness of waste stored in geologic repositories and could significantly reduce the potential consequences of the successful clandestine construction of a small-diameter tunnel into a repository, helping to deter such attempts in the first place. However, the recovery of only plutonium and uranium by reprocessing does not achieve the largest possible reduction in the attractiveness of the waste:

- Neptunium-237 has characteristics similar to those of highly enriched uranium (HEU) and, in principle, similar utility for nuclear explosives and is present at roughly 2% of the effective concentrations of plutonium, growing to 5% through the ^{241}Pu-^{241}Am decay chain.

- If ^{237}Np is recovered, it appears desirable to leave ^{243}Am in the waste stream as a gamma radiation barrier, in concentrations comparable to the residual plutonium concentrations, if plutonium separation occurs early enough to keep the ^{241}Am/^{243}Am ratio low.

- It is unlikely that reprocessing and recycling into light-water reactors and fast breeder reactor or accelerator transmutation systems can ever eliminate the need to dispose of some waste streams of attractiveness comparable to spent fuel. The primary advantage of designing fuel cycles that generate low-attractiveness waste streams would be to reduce the number of repositories that do require careful safeguards monitoring and the probability that successful clandestine diversion might occur in the future. These benefits for future generations must be weighed against added risks accepted by the current generation in the handling of separated materials.

An intriguing observation raised here is the potential for ^{243}Am to provide a long-term radiation barrier, while not materially increasing residual plutonium concentrations in wastes. Fuel cycles that would send americium with low ^{241}Am/^{243}Am ratios into waste could potentially reduce future proliferation risks and safeguards burdens significantly. Advanced proliferation-resistant recycle schemes deserve additional attention as routes that could reduce both current and future proliferation risks.

Deposition and Dynamic Response of Critical Deposits in Geologic Repositories

Working with other faculty members of the Department of Nuclear Engineering at U.C. Berkeley, Peterson has studied potential mechanisms for criticality in geologic repositories and the potential dynamic response of critical deposits. The study found that configurations exist of HEU and ^{239}Pu with rock and water that exhibit positive reactivity feedback, and therefore have the potential for significant energy release. However, for Yucca Mountain the study was also unable to identify chemical or hydrologic mechanisms with a significant probability of forming such configurations.

Two primary sets of problems remained to be resolved for repository autocatalytic criticality. The first relates to more comprehensive scenario development, to quantify the probabilities for the creation of critical deposits and to identify engineered systems to minimize such probabilities. For this work the event tree, already developed, has provided a useful tool.

The second set of topics relates to improved estimates of maximum energy release from overmoderated heterogeneous autocatalytic deposits. Modeling such systems requires numerical simulations coupling hydrodynamic and neutronic response. Key issues included resolving reactivity temperature coefficients (i.e., using sufficiently small energy groups for S_n methods or using Monte-Carlo methods) and using appropriate equations of state for moist rock, which correctly resolve both the solid behavior and the rock/water mixture behavior that occurs after the rock loses its mechanical integrity. The adopted approach is to use a code that had robust capabilities for coupled hydrodynamic and neutronics calculations and to develop new equations of state for moist tuff that correctly reflect the rock response in the low-temperature, low-pressure regime of such autocatalytic systems.

Neutronics calculations for plutonium deposited uniformly in moist, porous rock, indicate that such systems can possess positive reactivity temperature coefficients. If plutonium were continually added, or water removed, to the point where criticality occurred, fission heating would cause the system temperature and reactivity to rise. Because the negative reactivity feedback from solid thermal expansion can be small compared with the positive effect from system heating, the power excursion would then be terminated primarily by expansion from rock and water vaporization in small systems (<1-m radius) and by negative feedback as system temperatures exceed the plutonium resonance temperature in large systems (>1-m radius). This work performed coupled neutronics and hydrodynamics calculations for spherical plutonium systems with realistic equations of state, showing that energy released decreases rapidly with decreasing system radius. Although geochemical mechanisms can not naturally form such homogeneous plutonium deposits because of plutonium's low solubility, the results provide some insight for the potential response of more plausible heterogeneous plutonium colloid and HEU systems, where the dynamic response would be substantially more complex.

The calculations presented here used a Los Alamos code for coupled hydrodynamic and neutronics, applied to spherical, homogeneous deposits of plutonium in moist porous tuff rock. The reference case considered was a 1.83-m-radius homogeneous plutonium deposit in rock with 32% porosity, the pores filled to a saturation of 60% with water, giving a water weight fraction of 10% and a total density, including water, of 1888 kg/m^3. A new method for generating realistic nonequilibrium rock equation of state was developed (Fig. 2). Parametric studies for other rock equations of state and system diameters were also performed.

If plutonium is postulated to deposit uniformly in a large volume of moist rock, of about 2 m in effective radius, calculations performed here suggest that the resulting dynamic response would involve melting and vaporization of the bulk of the core volume, reaching temperatures of 5000 K and generating sufficient vaporized rock to make subsequent venting a potential concern. However, the calculations also show that the energy release declines very rapidly with decreasing system size, as shown in Fig. 3, and that natural processes that would deposit fissile material heterogeneously over tens of centimeters length scales would initiate much more benign criticality excursions in much smaller volumes, before large-scale accumulation could occur.

More realistic repository systems would involve heterogeneous deposition of plutonium colloids or HEU in fractures. Here, reactivity insertion rates

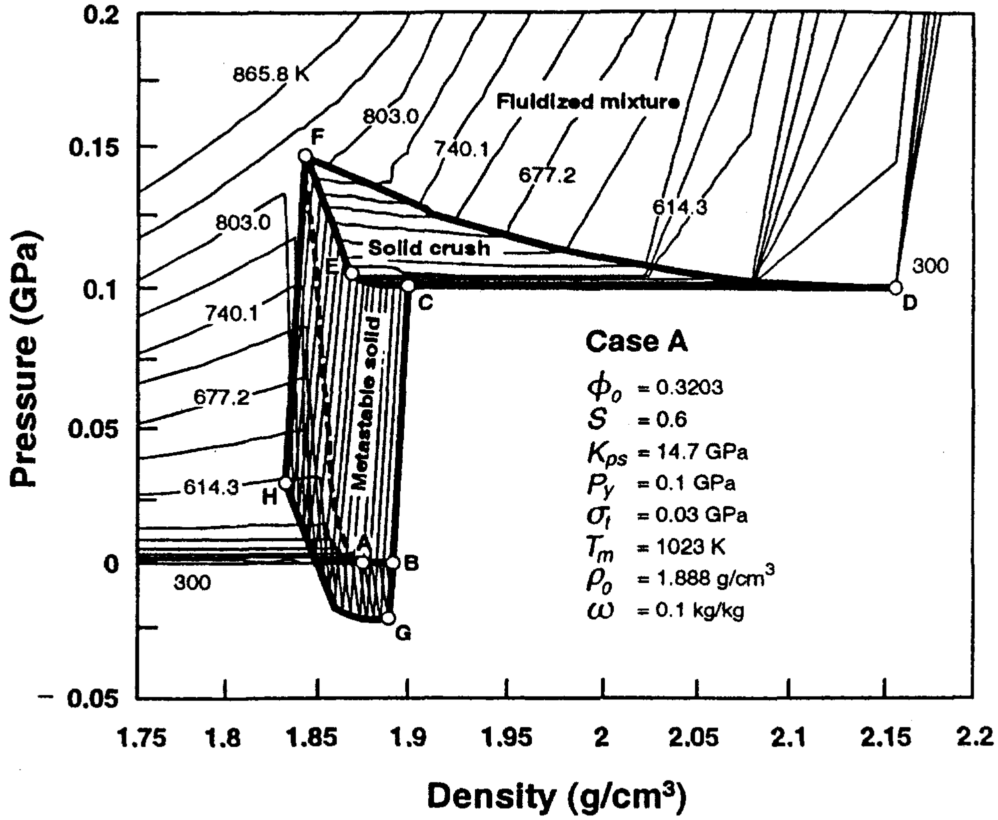
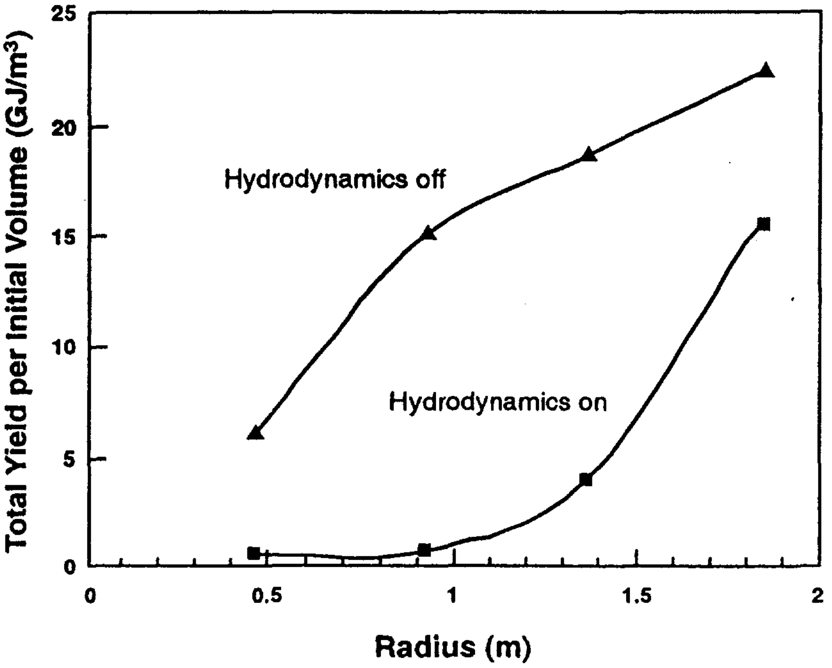


Fig. 2. Reference porous, moist rock equation of state created in this research effort.

Fig. 3. Energy release for the reference system scaled to smaller sizes, with hydrodynamics turned on and off. With hydrodynamics off, energy release is limited by the heating of the core region above the plutonium neutron-absorption resonance temperature.



would be limited by heat and mass transfer from fractures into the bulk rock and by rates of mixing of fissile material with moderator if melting occurs. These complex transport processes introduce substantial difficulty into modeling, and if conservative assumptions are made that these processes occur rapidly, the results would be similar to those reported here for homogeneous plutonium deposits because the total reactivity insertions from spectrum hardening, water expulsion, and homogenization are similar. The difficulty in modeling these more complex systems, with their uncertain geometry, suggests that the pragmatic basis for establishing repository criticality safety should rest on repository designs that preclude significant transport of plutonium or HEU from waste forms to surrounding geologic media.

Refereed Publications

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Peterson, P.F., "Issues for Detecting Undeclared Post-Closure Excavation at Geologic Repositories" (to be published in *Sci. Global Secur.*).

Peterson, P.F.l, and J.K. Kammerdiener, "Modeling of the Dynamic Response of Underground, Autocatalytic Systems" (submitted to *Nucl. Technol.*).

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Peterson, P.F., "Post-Closure Repository Safeguards: Comprehensive Assessments of Excavation Methods," International High-Level Radioactive Waste Management Conference, Las Vegas, NV, May 11–14, 1998 (invited).

Peterson, P.F., "Relative Proliferation Attractiveness of Reprocessing Waste and Spent Fuel: Implications for Long-Term Safeguards Technical Requirements," International Symposium on Energy Future in Asia/Pacific Region, Honolulu, HI,

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Texture Analysis from Time-of-Flight Neutron Diffraction Spectra

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Abstract

Electrons and x-rays are used routinely in every materials science laboratory to investigate properties of materials. Even though neutrons have distinct advantages, they are rarely applied. The main reason is that access to neutron sources, such as nuclear reactors and linear accelerators, has been very limited. Research has centered on a project to build a high-count-rate, general-purpose neutron diffractometer at the Los Alamos Neutron Science Center under the auspices of the University of California faculty. Of primary importance is that large sample volumes and thus properties of heterogeneous polycrystals, glasses, and liquids can be probed in situ, including those at high temperature and pressure. Diffraction spectra contain information on microstructure, internal stresses, and preferred orientation of crystals in aggregates, and new methods have been developed to extract information efficiently and quantitatively. The new instrument is of particular importance for the study of anisotropy in deformed materials that is due to preferred orientation of component crystals.

Background

A goal of materials science is to optimize properties for a particular performance. In the past much of this has been achieved with empirical experiments. More recently, as a result of better understanding of basic mechanisms, experiments have been replaced with simulations that capture the main ingredients of physical processes. The advantages of such an approach are that simulations are less costly and that simulations can be done for conditions that are not easily accessible for direct experimentation (time, pressure, temperature, and strain rates). In particular, time is a crucial parameter, for example, for estimating reliability of materials over long periods and for interpreting the history of materials from the present state. All simulations require not only an accurate description of acting mechanisms but also a calibration of these mechanisms. How does a reaction proceed with time? How does anisotropy develop during deformation? The answer to such questions must rely on quantitative materials characterizations and dynamic experiments. Both are still far from routine, even for very simple metal systems. The UCDRD-supported research was aimed at improving analytical methods by introducing neutron diffraction to mainstream materials science and testing new techniques with materials of low crystal symmetry, and composites. Data from such work will provide a firm basis for modeling efforts.

Progress

As part of this effort, the campus principal investigator (PI) has advanced the University of California materials research diffractometer (UCMRD), which has become known as HIPPO, for high pressure–preferred orientation. HIPPO was selected for rapid construction under the DOE-sponsored SPSS Project and is currently being built at Los Alamos and UC Berkeley. The PI also serves on this large funded equipment proposal, and the research in the analysis of neutron diffraction spectra has become an important basis, so that future users of the HIPPO facility can take full advantage once it becomes operational in the year 2000.

The HIPPO time-of-flight neutron diffractometer is designed for the study of properties of polycrystalline materials (including powders) and liquids. Of particular interest is the investigation of small (1-mm^3) and large (2-cm^3) sample volumes at high (2000-K) and low (10-K) temperatures at high pressure (20 GPa) and in different atmospheres. A flexible sample environment (large 75-cm-diam sample well) will accommodate ancillary equipment such as goniometers, furnaces, cryostats, straining stages, high-pressure cells, etc. The diffractometer will have main applications in the fields of phase transformations, high-pressure research, polycrystal anisotropy (texture-strain-stress), and complex materials (crystallography). It will be possible to study the dynamics of reactions, recrystallization, and deformation of bulk anisotropic samples at a wide range of temperature and pressure conditions. No existing instrument, worldwide, has this capability.

Advantages of neutron diffraction are mainly low absorption (applicable to large coarse samples, environmental stages) and high spectral resolution. The PI has worked for many years with scientists at the Los Alamos Neutron Science Center and the Intense Pulsed Neutron Source to develop new methods of texture analysis that take advantage of the unique properties of time-of-flight neutrons. First, two-dimensional position sensitive detectors were explored, but ultimately individual detector banks as implemented on powder diffractometers were preferred. This research and parallel investigations provided the basis for the design of the HIPPO diffractometer.

A diffraction spectrum can be explained on the basis of the incident beam, the physics of the diffraction process, instrument parameters (such as resolution), background, and the characteristics of the material. These characteristics include crystal structure (lattice, atomic positions, and thermal vibrations), the orientation distribution of crystallites in a polycrystal and microstructure (grain size and shape), and elastic strain. The crystallographic Rietveld method is an elegant approach to extract this broad information and was particularly expanded to include texture analysis. A multiplatform software, written in Java, is currently in a general state of testing. The goal has been to produce a user-friendly quantitative software system that is accessible to the average materials scientist who does not have much knowledge about crystallography and texture analysis.

The method has been applied to some systems that were chosen because of their general interest and because of specific properties that make them useful test cases. The first case is a two-phase metal composite, Cu-Fe, to evaluate changes in texture, microstructure, and strain during deformation and recrystallization. The second case is bulk high-temperature superconductors with extremely sharp textures and very complex diffraction spectra. The third case is peridotite, a polymineralic rock with weak-to-moderate textures. The components olivine (orthorhombic) and pyroxene (monoclinic) have low crystal symmetry. Peridotite is important to geophysicists because its deformation causes seismic anisotropy in the earth.

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Index of Investigators

Listed here are the principal investigators for the UCDRD projects described in this report, their affiliations, and the page numbers of their reports. Additional collaborators, postdoctoral fellows, and students are listed with each report. The principal investigators are from Los Alamos National Laboratory (LANL); the University of California ~~campuses~~ at Berkeley (UCB), Davis (UCD), Irvine (UCI), Los Angeles (UCLA), Riverside (UCR), San Francisco (UCSF), Santa Barbara (UCSB), and Santa Cruz (UCSC); and New Mexico universities, including New Mexico Highlands University (NMHU), New Mexico State University (NMSU), New Mexico Institute of Mining and Technology (NMT), and the University of New Mexico (UNM).

CULAR

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Kohler, Bryan E. (UCR),
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