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Brookhaven National Laboratory's

Annual Report of

Laboratory Directed Research & Development Program Activities For FY 2001

Director's Office

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
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Acknowledgments

The Laboratory Directed Research and Development (LDRD) Program is managed by Leonard Newman, who serves as the Scientific Director, and by Kevin Fox, Special Assistant to the Assistant Laboratory Director for Finance & Administration (ALDFA). Preparation of the FY 2001 report was coordinated and edited by Leonard Newman and Kevin Fox, who wish to thank D.J. Greco and Regina Paquette for their assistance in organizing, typing, and proofing the document. A special thank you is also extended to the Photography and Graphic Arts Group for their help in publishing. Of course, a very special acknowledgement is extended to all of the authors of the project annual reports and to their assistants.

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Introduction

Brookhaven National (BNL) Laboratory is a multidisciplinary laboratory that carries out basic and applied research in the physical, biomedical, and environmental sciences, and in selected energy technologies. It is managed by Brookhaven Science Associates, LLC, under contract with the U. S. Department of Energy. BNL's total annual budget has averaged about $450 million. There are about 3,000 employees, and another 4,500 guest scientists and students who come each year to use the Laboratory's facilities and work with the staff.

The BNL Laboratory Directed Research and Development (LDRD) Program reports its status to the U.S. Department of Energy (DOE) annually in March, as required by DOE Order 413.2, "Laboratory Directed Research and Development," March 5, 1997, and the LDRD Annual Report guidance, updated February 12, 1999. The LDRD Program obtains its funds through the Laboratory overhead pool and operates under the authority of DOE Order 413.2.

The goals and objectives of BNL's LDRD Program can be inferred from the Program's stated purposes. These are to (1) encourage and support the development of new ideas and technology, (2) promote the early exploration and exploitation of creative and innovative concepts, and (3) develop new "fundable" R&D projects and programs. The emphasis is clearly articulated by BNL to be on supporting exploratory research "which could lead to new programs, projects, and directions" for the Laboratory.

As one of the premier scientific laboratories of the DOE, BNL must continuously foster groundbreaking scientific research. At Brookhaven National Laboratory one such method is through its LDRD Program. This discretionary research and development tool is critical in maintaining the scientific excellence and long-term vitality of the Laboratory. Additionally, it is a means to stimulate the scientific community and foster new science and technology ideas, which becomes a major factor in achieving and maintaining staff excellence and a means to address national needs within the overall mission of the DOE and BNL.

The LDRD Annual Report contains summaries of all research activities funded during Fiscal Year 2001. The Project Summaries with their accomplishments described in this report reflect the above. Aside from leading to new fundable or promising programs and producing especially noteworthy research, the LDRD activities have resulted in numerous publications in various professional and scientific journals and presentations at meetings and forums.

All FY 2001 projects are listed and tabulated in the Project Funding Table. Also included in this Annual Report in Appendix A is a summary of the proposed projects for FY 2002. The BNL LDRD budget authority by DOE in FY 2001 was $6 million. The actual allocation totaled $5.3 million.

The following sections in this report contain the management processes, peer review, and the portfolio's relatedness to BNL's mission, initiatives and strategic plans. Also included is a metric of success indicators.

Management Process

PROGRAM ADMINISTRATION:

Overall Coordination: Overall responsibility for coordination, oversight, and administration of BNL's LDRD Program resides with the Laboratory's Director. Day-to-day responsibilities regarding funding, oversight, proposal evaluation, and report preparation have been delegated to the dedicated Scientific Director (SD) for the LDRD Program. The Office of the Assistant Laboratory Director for Finance & Administration (ALDF&A) continues to assist in the administration of the program. This includes administering the program budget, establishment of project accounts, maintaining summary reports, and providing reports of Program activities to the DOE through the Brookhaven Area Manager.

Responsibility for the allocation of resources and the review and selection of proposals lies with a management-level group called the Laboratory Directed Research & Development Program Committee. For Fiscal Year 2001, the Program Committee--which selected the 2002 programs--consisted of eight members. The Scientific Director of the LDRD Program chaired the Committee, and the other members were the Deputy Director (DD) for Science and Technology, four Associate Laboratory Directors (ALDs), and two members from the scientific departments and divisions (S).

2001 LDRD PROGRAM COMMITTEE

Leonard Newman	**Chairperson (SD)**
Peter Paul	**Science & Technology (DD)**
Creighton Wirick	**Energy, Environment & National Security (ALD)**
Thomas Kirk	**High Energy & Nuclear Physics (ALD)**
Nora Volkow	**Life Sciences (ALD)**
Richard Osgood	**Basic Energy Sciences (ALD)**
John Gatley	**Medical Science (S)**
Steven Hulbert	**National Synchrotron Light Source (S)**

Allocating Funds: There are two types of decisions to be made each year concerning the allocation of funds for the LDRD Program. These are: (1) the amount of money that should be budgeted overall for the Program; and (2) of this, how much, if any, should go to each competing project or proposal. Both of these decisions are made by high-level management.

For each upcoming fiscal year the Laboratory Director, on recommendation by the SD for LDRD and in consultation with the ALDF&A, develops an overall level of funding for the LDRD Program. The budgeted amount is incorporated into the Laboratory's LDRD Plan, which formally requests authorization from the DOE to expend funds for the LDRD Program up to this ceiling amount.

The majority of projects are authorized for funding at the start of the fiscal year. However, projects can be authorized throughout the fiscal year, as long as funds are available and the approved ceiling for the LDRD Program is not exceeded.

The actual level, which may be less, is determined during the course of the year and is affected by several considerations including: the specific merits of the various project proposals, as determined by

Laboratory management and the members of the LDRD Program Committee; the overall financial health of the Laboratory; and a number of budgetary tradeoffs between LDRD and other overhead expenses. At BNL the LDRD Program (see table below) has historically amounted to a much smaller portion of the total budget than at comparable National Laboratories. This prevented the Laboratory from preparing itself for work in emerging areas of research. Accordingly, this fraction of LDRD funds is being increased with a target of about 4%, which is still significantly less than the DOE mandated maximum of 6%.

LDRD COSTS VS. TOTAL LABORATORY COSTS

operating $ in millions

FISCAL YEAR	DOE FUNDS	WFO FUNDS	TOTAL FUNDS	LDRD FUNDS	% OF TOTAL
1985	153.0	40.4	193.1	1.82	0.9
1986	156.5	45.1	201.6	2.52	1.2
1987	161.7	45.6	207.3	1.44	0.7
1988	176.7	45.9	222.6	1.51	0.7
1989	193.6	46.7	240.3	2.67	1.1
1990	203.8	45.2	249.0	1.94	0.8
1991	220.9	50.3	271.2	1.32	0.5
1992	234.3	47.2	281.5	1.87	0.7
1993	231.4	47.3	278.7	2.01	0.7
1994	237.0	47.9	284.9	2.32	0.8
1995	243.0	53.7	296.7	2.48	0.8
1996	251.6	50.6	302.2	3.05	1.0
1997	257.2	52.5	309.7	3.46	1.1
1998	251.8	49.5	301.3	2.56	.8
1999	294.1	48.1	342.2	4.53	1.3
2000	343.0	58.0	401.0	5.58	1.4
2001	309.4	75.6	385.0	6.00	1.4
2002	290.0	74.4	364.4*	7.00	1.9

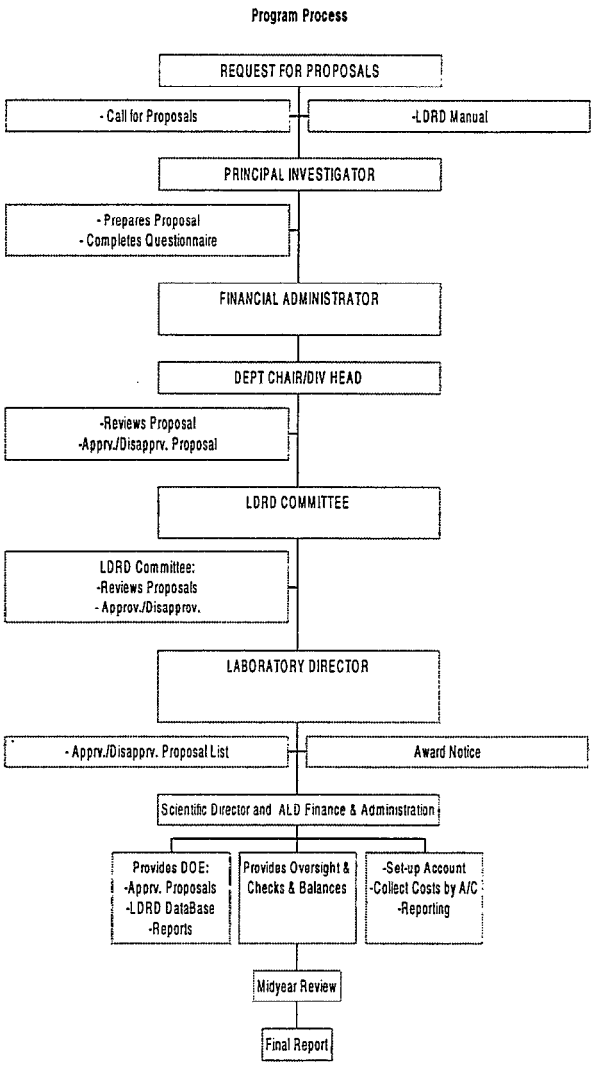
*Estimated only

Request for Proposals: The availability of special funds for research under the LDRD Program is well publicized throughout the Laboratory. This is done using two methods --one occurring at yearly intervals, the other occurring irregularly. Each year a call memorandum is sent by the SD for LDRD to all the Associate Laboratory Directors and Department Chairpersons. The FY 2002 call memorandum issued in January 2001 is attached as Exhibit A. For FY 2001 this call memorandum was issued in January 2000. This early schedule better facilitated the recruitment of post-doctorate candidates to support LDRD projects. Both memorandums reference the BNL LDRD Manual, which is available to all employees on the web at https://sbms.bnl.gov/ld/ld03/ld03d011.htm. (Exhibit C) The other method is through a feature article in The Bulletin, the Laboratory's weekly newspaper.

The LDRD Manual specifies the requirements necessary for participation in the program. It states the program's purpose, general characteristics, procedures for applying, and restrictions. An application for funding, i.e., a project proposal, takes the form of a completed "Proposal Information Questionnaire," Exhibit D. An application must be approved up the chain-of-command which includes the initiator's Department or Division Budget Administrator and the Department Chairperson or Division Head. Plans to ensure the satisfactory continuation of the principal investigator's regularly funded programs must also be approved. The applications are then forwarded to the LDRD Program Committee for full review and consideration for funding.

The process that solicits and encourages the development of proposals has evolved into two modes of operation. Specifically, the ideas for proposal development may originate

among the scientific staff in response to the general call for proposals. Alternatively, they



may be initiated by Laboratory science management. Eventually, both follow the

standard procedures for proposal approval up the chain-of-command to the same decision makers. The fact that all proposals must be approved up the chain-of-command permits BNL managers to consider all ideas together when designing the mix of projects for the LDRD Program.

An initiative from management typically takes the form of a broad topical area or item of special interest such as nanoscale science. Then ideas are communicated to scientific staff members who are known to be in a position to pursue and develop the idea in the form of a more formal proposal.

Proposal Review: Once the cognizant line managers approve the proposals, they are forwarded to the Chairperson of the Committee (SD for LDRD) who transmits a copy of all proposals received to the Committee for review. The Committee considers all proposals that have met certain minimum requirements pertaining to the Department's and BNL's LDRD policies.

Lead proponent responsibility of a proposal is assigned to that Associate Laboratory Director of the Committee who oversees and directs the technical area from which the proposal originated. A description of the process is outlined in Exhibit B. All members have several weeks to review the proposals and prepare for the full debate of the proposal.

Selection Criteria: Minimum requirements of each proposal are: (1) consistency with program purpose; (2) consistency with missions of BNL, DOE, and NRC; (3) approval by Department Chairperson and/or Division Head, and cognizant Associate/ Assistant Director; (4) assurance of satisfactory continuation of principal investigator's regularly funded programs; (5) modest size and general scheduled for 2 years but limited to no more than 3 years; (6) will not substitute for, supplement, or extend funding for tasks normally funded by DOE, NRC, or other users of the Laboratory; (7) will not require the acquisition of permanent staff; (8) will not create a commitment of future multi-year funding to reach a useful stage of completion; and (9) will not fund construction line-item projects, facility maintenance, or general purpose capital equipment.

The selection criteria used to evaluate and rank individual proposals are stated in broad terms. While the LDRD Manual clearly states that selection is based on (1) scientific or technological merit, (2) innovativeness, (3) compliance with minimum requirements, (4) proposal cost as compared to the amount of available funding, and (5) its potential for follow-on funding. The requirements of DOE Order 413.2 are also carefully considered during the selection process to ensure that proposals are consistent with DOE criteria.

Project Approval: After all presentations are heard, the Committee selects the highest priority proposals by concurrence. Differences, if any, are resolved by the Chairperson. Some funding may be held in reserve during the earlier meetings of the fiscal year so that funds remain available for proposals submitted at later dates. The funding amount requested in any one specific proposal may be changed or adjusted during the approval process. The Committee's recommendation is then submitted to the Laboratory Director for his approval. The ALDF&A then sets up a separate laboratory overhead account to budget and collect the costs for the project.

Project Supervision: The SD for LDRD carries out overall supervision of the projects. Supervision over the actual performance of LDRD projects is carried out in the same way as other research projects at the Laboratory. Each principal investigator is assigned to an organizational unit (Department, Division), that is supervised by a chairperson or manager.

Each chairperson or manager is responsible for seeing that the obligations of the principal investigator are satisfactorily fulfilled and that the research itself is carried out according to standard expectations of professionalism and scientific method. The SD for LDRD monitors the project's status, schedule, and progress and coordinates with the chairperson or manager as necessary.

The SD for LDRD organizes a mid-year review of all projects. Each PI presents a progress report on the status of their project. In attendance will be the SD for LDRD, the DD, the cognizant ALD and Department Chair, and a representative from the ALDF&A and DOE-BAO. This review checks on the progress of the projects including its funding schedule. This allows the SD for LDRD to ensure that the work is being completed in a timely manner.

In addition, the SD for LDRD conducts a monthly meeting with the DOE Brookhaven Area Office to update the progress of the program and to solicit assistance to verify that the BNL LDRD Program is meeting the overall LDRD requirements. This includes providing the DOE Brookhaven Area Office with copies of all funded proposals, an LDRD Program database, and a project funding and schedules summary report.

Project Reporting: Routine documentation of each project funded under the LDRD Program consists of a file containing: (1) a copy of the written proposal; (2) all interim status reports; (3) notifications of changes in research direction, if any; and (4) reports on costs incurred. Also, a formal LDRD Plan and the Annual Report on the LDRD Program (this Report) are submitted to BNL management and the DOE summarizing work progress, accomplishments, and project status on all projects.

Documentation for the overall Program consists of (1) various program history files, (2) a running list of all proposals with their

acceptance/rejection status, (3) funding schedule and summary reports for all approved projects, (4) permanent records on cost accounting, and a database containing information on each funded project (description, funding by fiscal year, status and accomplishments, follow-on funding, publications, etc.).

Some of the projects involve animals or humans. Those projects have received approval from the Laboratory's appropriate review committees. The projects which involve animals or humans are identified in this report as follows:

Note: This project involves animal vertebrates or human subjects.

This is noted on the summary sheet and also at the end of each report.

Peer Review

LDRD projects have peer reviews performed in several different ways. Primarily, LDRD research is managed and reviewed by the cognizant Department and Division manager. These projects are a part of the activities of their respective Department and Divisions in which they reside. The BNL LDRD Program itself does not solicit formal peer reviews, consisting of written comments by experts outside the normal lines of supervision. Instead, advisory committees that consist of subject matter experts from academia and industry conduct peer reviews of LDRD projects as part of a department 's program review. One such group is the Brookhaven Science Associates' Science Advisory Committee, which performs peer reviews of different Laboratory programs on a rotating basis. There are also periodic reviews of the science at the Laboratory performed by various offices of DOE.

In addition to these outside peer reviews of the BNL program, the members of the LDRD Committee are considered to have sufficient technical knowledge to perform peer reviews of projects during the initial selection process and annual renewal. Also, all LDRD projects go through a formal mid-year review (described in the previous section under project supervision) conducted by the SD of the LDRD Program that includes the cognizant Department Chair and Associate Laboratory Director.

Results: The BNL LDRD Program clearly has a vested interest in performing peer reviews in order to maintain a high caliber of research. The results of these reviews are included in the BNL Year End Self-Evaluation for Fiscal Year 2001. Details of this process are given below.

Brookhaven Science Associates (BSA) operates BNL utilizing a Performance-Based Management System (PBMS). The PBMS is designed to include a hierarchy of clear, reasonable, and objective performance measures as standards to assess BSA's overall performance of scientific, technical, operational, community, and managerial (and communications) obligations.

Specifically, in FY 2001 BNL had four critical outcomes in the BSA Contract. The most important critical outcome was Excellence in Science and Technology. Under this critical outcome was an objective entitled Quality of Research. LDRD projects were included in the self-evaluation for this objective.

In the evaluation process the Associate Laboratory Directors (ALDs) of the four BNL Science Directorates assigned self-evaluation scores for each of the four Critical Outcome Objectives, which are Quality of Research, Relevance to DOE Mission and National Need, Success in Construction and Operation of Research Facilities, and Effectiveness and Efficiency of Research Program Management. In determining the evaluation scores the ALDs considered many factors, including bench-marks from past experience and DOE evaluations, major successes such as the RHIC startup and hiring of scientific staff, peer review input, and on the negative side research program deficiencies, such as the conditions that warranted the human subjects research program stand-down.

For FY 2001, the performance under this Critical Outcome was an Outstanding with an overall score of 3.54 out of a possible 4.0.

Self Assessment

BNL supports the concept of continued improvement as part of its management of the Laboratory. To achieve this goal every year BNL performs self assessments on various functions at the Laborotory. In FY 2001, BNL performed a self assessment on the LDRD Program administration. This self assessment of BNL's LDRD Program administration was based on the Malcolm Baldrige National Quality Award Criteria for 1998. The assessment detailed the LDRD's administration strengths and opportunities for improvement (OFI) for each criterion identified.

The overall summary of the assessment's strengths and opportunities for improvement are as follows:

Summary of Strengths:

The LDRD Program has a good customer satisfaction rating. The customer survey revealed that on average 65% of those that responded gave a favorable review of the administration of the LDRD Program. Whereas only 16% gave a Disagree or Tend to Disagree rating.

In FY 2001, the SD for LDRD was hired which added to the internal control as well as strength the overall program.

The FY 2002 LDRD Plan was submitted to DOE in August of 2001 for review. In October of 2001 the 2002 Plan was approved, and DOE-HQ informed the DOE-BAO that the plan was an excellent document showing vast improvement from the prior year.

The favorable customer satisfaction is a result of the SD of the LDRD and ALDF&A staff being knowledgeable and making themselves readily available and responding promptly to customer inquiries. Communication within the group is very good. Every effort is made to update and streamline processes and procedures.

Summary of Opportunities for Improvements:

The areas identified below as opportunities for improvement will only enhance current operations. None are considered major.

1. Convert the legacy LDRD policy to the correct Standard Based Management System format

2. Collect data from projects after their completion to support success indicators

3. Increase awareness of the LDRD Program to the Laboratory scientific community

This self assessment contained meaningful recommendations and will be utilized to improve the LDRD Program at Brookhaven.

Relatedness of LDRD to Laboratory Programs and Initiatives

BNL's mission is to produce excellent science in a safe, environmentally benign manner with the cooperation, support, and appropriate involvement of our many communities. Brookhaven was founded as a laboratory which would provide specialized research facilities that could not be designed, built, and operated at a university or industrial complex, and provides a scientific core effort for these facilities. This still remains a basic mission of the Laboratory.

BNL is committed to cultivating programs (including the LDRD) of the highest quality. These programs address DOE's Strategic Mission which is to conduct programs relating to energy resources, national nuclear security, environmental quality, and science.

Brookhaven National Laboratory has the following four elements in its mission which support the four DOE programmatic business lines.

RESEARCH FACILITIES

Conceive, design, construct, and operate complex, leading-edge, user-oriented facilities in responsive to the needs of the DOE, and the needs of the international community users.

SCIENTIFIC RESEARCH

Carry out basic and applied research in long-term high risk programs at the frontier of science.

TECHNOLOGY DEVELOPMENT

Develop advanced technologies that address national needs and to transfer them to other organizations and to the commercial sector.

KNOWLEDGE TRANSFER

Disseminate technical knowledge to educate new generations of scientists and engineers, to maintain technical capabilities in the nation's workforce, and to encourage scientific awareness in the general public.

Research Facilities and Scientific Research have a synergistic relationship. To maintain and constantly improve a research facility and to keep it at the cutting edge, it is essential that the Laboratory have a significant research staff of excellent stature. The staff drives the performance of the facility. Having several complementary facilities at one location, such as the National Synchrotron Light Source and the Alternating Gradient Synchrotron, allows unique research capabilities. The other two elements of the Laboratory's mission--Technology Development and Knowledge Transfer-- bridge all of the research facilities and research programs.

The four elements of Brookhaven's mission support and cut across the four central activities of the Department of Energy as defined in its Strategic Plan.

The Laboratory's breadth of expertise as delineated in Table 1 and 2 provides the basis for its contributions to the DOE's missions and focuses on providing extraordinary tools for the pursuit of basic science and technology.

Table 1 - Expertise Derived from Brookhaven's Core Competencies – Science

High Energy and Nuclear Physics:
- Rare kaon decays
- Muon anomalous magnetic moment
- Exotics and glueball spectroscopy
- Strange matter
- Solar neutrinos
- Nuclear matter in extremes of temperature and density
- QCD phase transitions

Advanced Accelerator Concepts:
- Short wavelength accelerating structures
- Production of coherent radiation free electron laser
- Muon collider and storage ring
- Neutron Sources
- Interlaboratory collaboration on the design and construction of the Spallation Neutron Source

Materials Sciences:
- High Tc superconductivity
- Magnetism
- Surface studies-catalysis, corrosion and adhesion
- Condensed matter theory: metallic alloys and correlated electron systems
- Materials synthesis and characterization with neutron- and X-ray diffraction
- Structure and dynamics
- Defect structure

Chemical Sciences:
- Dynamics, energetics, reaction kinetics on the pico-second time scale
- Thermal-, photo- and radiation-reactions
- Catalysis and interfacial chemistry
- Homogeneous catalysis with metal hydrides
- Porphryin chemistry
- Electrochemistry

Environmental Sciences:
- Global change
- Atmospheric chemistry
- Marine science
- Soil chemistry
- Cycling of pollutants
- Environmental remediation

Medical Science:
- Medical imaging: PET, MRI, SPECT, Coronary Angiography
- Nuclear medicine
- Radionuclides, radiopharmaceuticals, synthesis and application
- Advanced cancer therapies: neutron capture, microbeam radiation, proton radiation, photon-activation therapy
- Mechanisms of oncogenesis

Molecular Biology and Biotechnology:
- Genome structure, gene expression, molecular genetics
- DNA replication, damage and repair
- Structure and function of enzymes, protein engineering
- Plant genomics, biochemistry and energetics
- Solution structure, kinetics and interaction of biomolecules
- Biostructure determination by X-ray and Neutron scattering
- Biostructure determination and mass measurements by electron microscopy

Advanced Scientific Computing and Systems Analysis:
- Atmospheric Transport Modeling
- Infrastructure assessment
- Energy modeling
- Groundwater modeling
- Intelligent sensor and security systems

Table 2 - Expertise Derived from Brookhaven's Core Competencies - Technology

Physical, Chemical and Materials Science:

- Advanced instrumentation and devices for precision electronics, optics and microelectronics
- Superconducting and magnetic materials
- Micromachining
- Battery technology
- Permanent magnets
- "Designer" polymers

Accelerator Technology:

- High-field, high-quality superconducting magnets
- High-power radio-frequency systems
- Ultrahigh vacuum systems
- Advanced accelerator designs
- Accelerator/spallation source applications
- Insertion device development: wigglers and undulators
- High-power, short-pulse lasers

Medical Technologies:

- Biomedical applications of nuclear technology
- Development and production of radio-nuclides/radiopharmaceuticals
- Development of particle and X-ray radiation therapies for cancer
- Medical imaging
- X-ray microbeam therapy

Biotechnology:

- Neutron and synchrotron x-ray scattering
- Large scale genome sequencing
- High resolution scanning and cryogenic electron microscopy
- Cloning, expressing and engineering genes
- Metal cluster compounds for electron microscope labels
- Phage displays for probing specific interactions
- Biocatalytic treatment of heavy oils

Environmental and Conservation Technologies:

- Ultra sensitive detection and characterization
- Environmental remediation and mitigation
- Waste treatment
- Disposal of nuclear materials
- Energy-efficiency technologies
- Fuel cell technologies
- Infrastructure modernization
- Transportation: Intelligent transportation systems, MAGLEV, RAPTOR
- Radiation protection
- Bioremediation technologies

Safety, Safeguards, and Risk Assessment:

- Safeguards, non-proliferation and arms control
- Design and development of non-proliferation reactors and fuel cycles
- Material and component survivability testing
- Remote sensing of chemical signatures
- Technical support for U. S. policy
- Safety analysis of complex systems
- Probabilistic risk assessment and management
- Human factors
- Energy-system modeling
- Structural, thermal hydraulics and nuclear design
- Integrated Safety Management

The following is a list of themes that are derived from the breadth and expertise expressed in Tables 1 and 2. The number of LDRD projects as related to these BNL themes is shown in Table 3.

Table 3 - THEMES

	THEMES	Number of LDRD Projects
1	Scientific Facilities Operations • RHIC • AGS • NSLS • ATF • LEAF • STEM • Tandem • BMRR	**0**
2	Nuclear Physics • Quark/gluon plasma • Spin Physics	**1**
3	High Energy Physics • Standard Model • Rare Particles & Processes	**0**
4	Advanced Accelerator & Detector Concept and Designs - Advanced Instrumentation • Muon Collider • DUV-FEL • LHC • SNS	**20**
5	The Physics & Chemistry of Materials • Superconductivity • Magnetism • Surfaces • Nanostructure	**21**
6	Energy Sciences • Combustion • Catalysis • Bio-fuels • Batteries • Geothermal • Buildings	**12**
7	Environmental Sciences • Atmospheric • Terrestrial • Bio-remedial • Waste Technologies	**7**
8	Medical and Imaging Sciences & Technology	**6**
9	Advanced Computation	**0**
10	Biological Sciences	**13**
11	Critical Infrastructure	**1**
Totals		**82***

*The total number is greater than the number of LDRD Projects since some projects come under more than one theme.

Overall, the LDRD portfolio supports all of the BNL themes and strategic objectives which in turn supports the DOE strategic initiatives.

Summary of Metric Data

Statistical data is collected on all projects for the annual report. Since the LDRD Program is intended to promote high-risk research, the data collected has nominal value on a project-by-project basis. It does provide a general overall picture of the LDRD Program productivity.

Some of the more common indicators/ measures of success are: 1) the number of proposed, received and approved projects, 2) amount of follow-on funding, 3) the number of patents applied for, and 4) the number of articles published in peer-reviewed journals.

Historically, statistics on the number of projects approved, compared to those rejected, show an overall approval rate of about 30 percent for new starts. Ten scientific departments were represented in the FY 2001 LDRD Program. From inception of the program through September 2001 (for FY 2001), 918 project proposals were considered and 294 were approved. These show and demonstrate that the LDRD Program at BNL is expanding and is generating interest from across the entire Laboratory population.

In FY 2001, the BNL LDRD Program funded 70 projects, 29 of which were new starts, at a total cost of $5,345,436. Included in this report is the Project Funding Table, which lists all of the FY 2001 funded projects and gives a history of funding for each by year.

FISCAL YEAR	AUTH K$	COSTED K$	NO. REC'D	NEW STARTS
1985	1,842	1,819	39	13
1986	2,552	2,515	22	15
1987	1,451	1,443	29	8
1988	1,545	1,510	46	14
1989	2,676	2,666	42	21
1990	2,008	1,941	47	9
1991	1,353	1,321	23	14
1992	1,892	1,865	30	14
1993	2,073	2,006	35	14
1994	2,334	2,323	44	15
1995	2,486	2,478	46	13
1996	3,500	3,050	47	17
1997	4,500	3,459	71	10
1998	4,000	2,564	53	4
1999	4,612	4,526	67	25
2000	6,000	5,534	93	21
2001	6,000	5,345	97	38
2002	7,000	---	87	29
TOTALS	57,046	46,413	918	294

An analysis of the FY 2001 projects shows that many of the projects were reported to have submitted proposals for grants or follow-on funding (several received funding), and a multitude of articles or reports were reported to be in publication or submitted for publication. Several of these projects have already experienced varying degrees of success, as indicated in the individual Project Program Summaries that follow. The complete summary of success indicators is as follows:

SUCCESS INDICATORS	QTY
Total number of proposals submitted for follow-on funding (other than LDRD).	63
Total Number of projects that all or part of the research performed continue (with or without interruption) under other auspices.	26
Total number of referred publications based on the work supported by LDRD funds and done during the active period of this project.	105
Total number of students and postdocs (combined total as FTEs) directly supported by this LDRD project while this project was active.	55.7
Total number of new, permanent, full-time staff hired as a direct result of this LDRD Project.	7
Total number of (non-publication) copyrights derived both directly from this LDRD project and from any follow-on efforts to date.	0
Total number of invention disclosures submitted to the Laboratory's Office of Intellectual Property & Industrial Partnership that were derived either from this LDRD project directly or from any follow-on efforts to date.	8
Total number of patent applications either applied for or granted that were either derived from this LDRD project directly or from any follow-on efforts to date.	3
Total number of review presentations that pertain to this work.	35

NOTE: Total number means sum total for all years of the project

In conclusion, the overall LDRD Program has been successful. In FY 2001, the LDRD Program has maintained the level established in FY 2000, which was a significant increase from FY1999. This increase in size is a consequence of the identification of the LDRD Program by Laboratory Management to be an important part of its future. The LDRD Program is a key component for developing new areas of science for the Laboratory. In FY 2001 alone the Laboratory has experienced a significant scientific gain by the achievements of the LDRD Projects.

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2001

LDRD Proj. No.	Project Title	P.I.	Dept./Bldg.	Theme	Actual FY 99$	Actual FY 00$	Actual FY 01$	Approved Budget FY 02$	RequestedBudget FY 03 $	Total
98-23A	Performance Enhancement in a Photoinjector Electron Linac	E.Johnson	NSLS/725D	4	$300,339	$266,298	$250,429			$817,066
98-23B	Pulse Compression and Emittance Preservation in a High Brightness Electron Linac	W. Graves	NSLS/725D	4	$150,621	$133,000	$130,213			$413,834
99-01	Ultra-fast Detector Based on Optical Techniques	Y.Semertzidis	PHYS/510A	4	$113,345	$88,932	$75,898			$278,175
99-41	Efficacy of Unidirectional Microbeam Radiation Therapy in Treating Malignant Tumors: Preclinical Studies in Rats and Mice	A. Dilmanian	MED/490	8	$119,571	$149,204	$127,877			$396,652
99-46	Experimental and Theoretical Investigation of Transition Metal Oxides	J. Hill	PHYS/510B	5	$84,381	$61,969	$58,474			$204,824
99-51A	High Gain FEL Amplifier	G. Rakowsky	NSLS/725D	4	$372,668	$100,000	$182,871			$655,539
99-51B	Deep Ultra-Violet Free Electron Laser Optimization	E. Johnson	NSLS/725D	4	$124,222	$298,107	$180,742			$603,071
99-53	Development of High Brightness Electron Sources	I. Ben-Zvi	NSLS/725C	4	$201,393	$199,807	$98,349			$499,549
99-56	Attosecond Pulse Generation in High Harmonics	L. DiMauro	CHEM/555A	4	$109,251	$77,988	$71,812			$259,051
99-62	Studies of Catalysts for SOx and NOx Decomposition Using Synchrotron Radiation	J. Rodriguez	CHEM/555A	6	$121,957	$48,789	$57,458			$228,204
00-06	Probing Extreme QCD: Articulating the Physics Goals of an Electron-Relativistic Heavy Ion Collider (eRHIC) at BNL	R. Venugopalan	PHYS/510A	2		$83,928	$69,851	$0		$153,779
00-25A	Rapid Real-time Measurement of Aerosal Chemical Composition	Y.-N. Lee	Env. Sci./815E	7			$118,156	$121,000		$239,156
00-25B	Novel Techniques to Measure Aerosols and Aerosol Precursors: Multiple Humidity Tandam Differental Mobility Analyzer(TDMA)	F. Brechtel	Env. Sci./815E	7			$117,080	$121,000		$238,080
00-27	Nanocomposites of Silicon Polymorphs and Related Semiconductor Systems	D. O. Welch	MA/480	5		$79,117	$59,505	$0		$138,622
00-32	Microvascular Endothelial Cells as Targets for Ionizing Radiation	L. Pena	MED/490	8		$82,633	$100,622	$60,000		$243,255
00-40	The Structure of Membrane Proteins: Monolayers and Thin Films	B. Ocko	PHYS/510B	10		$16,566	$636	$50,400		$67,602
00-43	Understanding the Pathways of Ubiquitin Dependent Proteolysis	M. Bewley	BIO/463	10		$244,247	$216,260	$215,000		$675,507
00-44	Structural Characterization of DNA-PK, A Human DNA Double-Strand	J. M. Flanagan	BIO/463	10		$44,132	$73,550			$117,682
00-45	New Protein Expression Tools for Proteomics	P. L. Freimuth	BIO/463	10		$41,698	$109,754	$111,000		$262,452

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2001

LDRD Proj. No.	Project Title	P.I.	Dept./Bldg.	Theme	Actual FY 99$	Actual FY 00$	Actual FY 01$	Approved Budget FY 02$	RequestedBudget FY 03 $	Total
00-47	High-Throughput Structure Determination of the Human Proteome Project	F. W. Studier	BIO/463	10		$575,570	$284,443	$0		$860,013
00-49	Design Study of a Solid Target for Spallation Neutron Sources	J. Hastings	NSLS/725D	4		$301,241	$90,921	$0		$392,162
01-07	Development of Superconducting Accelerator Magnets Capable of High dB/dt	A. Ghosh	SUPERCONDUCT MAGNET DIV/ 902A	4			$143,588	$145,000	$156,000	$444,588
01-11	Combination of Magnetic Fields and 20 keV Synchrotron X-rays to produce Microbeams for Cell Culture Experiments	L. Pena	MED/490	10			$11,169	$11,400		$22,569
01-12	Gene Expression Profiling of Methamphetamine-Induced Toxicity in Neurons in Culture Using DNA Microassays	M. Vazquez	MED/490	8, 10			$105,192	$99,800		$204,992
01-13	"Functional Spectral Signature" (FSS) Method for Signal to Noise-Enhancement of Brain Patterns in PET Images	C. Felder	MED/490	8			$85,941	$86,100		$172,041
01-18	Exploration and Development of Ultrafast Single Short Detection Methods for Use with Pulse Radiolysis Experiments at LEAF	A. R. Cook	CHEM/555A	4			$62,401	$65,000	$65,000	$192,401
01-19	Metal NanoClusters and Electron Transfer in One, Two, and Three Dimensions (NANO III)	C. Creutz	CHEM/555A	5			$81,202	$145,000	$145,000	$371,202
01-20	Molecular Wires for Energy Conversion and Nano-Electronics	J. R. Miller	CHEM/555A	5, 6			$47,655	$50,000	$51,000	$148,655
01-21	Nanoscale Catalysts: Preparation, Structure and Reactivity (NANO II)	J. Hrbek	CHEM/555A	5, 6			$76,395	$80,000	$80,000	$236,395
01-23	Experimental and Theoretical Studies of the Formation of Titanium-Carbon Nanoclusters (NANO II)	T. Sears	CHEM/555A	5, 6			$103,067	$107,000	$107,000	$317,067
01-24	Development of a UV-Raman, Near-field Scanning Optical Microscope for *in-situ* Studies of Chemical Intermediates on Metal Nanoparticles (NANO II)	M. G. White	CHEM/555A	4, 5			$96,203	$100,000	$100,000	$296,203
01-26	Nanoscience Interests (NANO II)	J. Z. Larese	CHEM/555A	5			$28,333	$0	$0	$28,333
01-28	Development of New Techniques for Improvements in PET Imaging of Small Animals and Other Applications	D. Schlyer	CHEM/555A	8			$86,322	$90,000	$90,000	$266,322
01-30	Development of CZT Array Detector Technology for Synchrotron Radiation Applications	D. P. Siddons	NSLS/725D	4			$106,592	$107,000	$160,000	$373,592

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2001

LDRD Proj. No.	Project Title	P.I.	Dept./Bldg.	Theme	Actual FY 99$	Actual FY 00$	Actual FY 01$	Approved Budget FY 02$	RequestedBudget FY 03 $	Total
01-31	New Applications of Circular Polarized VUV-light (NANO IV)	E. Vescovo	NSLS/725D	4			$23,860	$45,000	$50,000	$118,860
01-32	Soft X-Ray Magnetic Speckle (NANO IV)	C. Sanchez-Hanke	NSLS/725D	4, 5			$41,173	$45,000	$50,000	$136,173
01-35	Prototype approaches for Infrared Nanospectroscopy	G. L. Carr	NSLS/725D	4, 5			$33,689	$45,000	$50,000	$128,689
01-36	Pressure-Induced Protein Folding Monitored by Small Angle X-Ray Scattering and Fourier Transform Infrared Microspectroscopy	Lisa Miller	NSLS/725D	10			$43,499	$45,000	$50,000	$138,499
01-38	Soft Condensed Matter Probed by Low-Energy Resonant Scattering	W. Caliebe	NSLS/725D	5			$32,873	$45,000	$50,000	$127,873
01-39	Femto-Seconds Electron Microscope Based on the Photocathode RF Gun	X. J. Wang	NSLS/725C	4			$145,593	$60,000	$0	$205,593
01-45	First-Principles Theory of the Magnetic and Electronic Properties of Nanostructures (NANO IV)	M. Weinert	PHYS/510A	5, 9			$88,387	$90,000	$91,000	$269,387
01-50	Cryo-EM for Solving Membrane Proteins	J. F. Hainfeld	BIO/463	4			$115,949	$118,000		$233,949
01-51	Human DNA Damage Responses: DNA-PK and p53	C. W. Anderson	BIO/463	10			$167,158	$168,000		$335,158
01-52A	Molecular Mechanisms Underlying Structural Changes in the Adult Brain: A Genetic Analyses	J. J. Dunn	BIO/463	8, 10			$117,218	$117,000		$234,218
01-58A	Catalytic Microcombustion Systems	C. R. Krishna	ES&T/526	5, 6			$93,108	$96,000		$189,108
01-59A	Power Quality and Reliability in Interconnected Microgrids	T. Butcher	ES&T/526	7, 11			$72,412	$0		$72,412
01-62	Mapping Electron Densities in Porphyrin Radical Crystals Using the NSLS	K. M. Barkigia	MA/555	6			$29,102	$70,000	$102,000	$201,102
01-67	High Sensitivity Mass Spectrometer	P. E. Vanier	NNS/197C	4, 7			$117,574	$121,000		$238,574
01-78	Development and Application of Cavity Ringdown Spectroscopy to the Detection and Monitoring of Trace Chemical Species in the Atmosphere	A. J. Sedlacek	Env. Sci./703	4, 7			$86,743	$90,000		$176,743
01-79	Development of a High Field Magnet for Neutrino Storage Rings	R. Gupta	SUPERCONDUCTMAGNET DIV/ 902A	4			$98,066	$100,000	$125,000	$323,066
01-82	DNA-Nano Wires that AutoConnect in 3 Dimensions (NANO III)	J. F. Hainfeld	BIO/463	5, 10			$58,814	$60,000		$118,814
01-85	Carbon Nanotube Chemical Probes for Biological Membrane Attachment Quantification (NANO III)	B. Panessa-Warren	Instru./ 535B	5, 10			$48,378	$49,800	$48,100	$146,278

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2001

LDRD Proj. No.	Project Title	P.I.	Dept./Bldg.	Theme	Actual FY 99$	Actual FY 00$	Actual FY 01$	Approved Budget FY 02$	RequestedBudget FY 03 $	Total
01-86	Self-organized Nanoparticles for Probing Charge Transfer at Metallic/Organic Interfaces (NANO III)	M. Strongin	PHYS/510B	5, 6			$46,504	$50,000	$50,000	$146,504
01-87	Charge Transfer on the Nano Scale: Theory (NANO III)	M. D. Newton	CHEM/555A	5, 6			$43,063	$55,000	$55,000	$153,063
01-88	Charge Transport through Dye-Sensitized Nanocrystalline Semiconductor Films (NANO III)	B. Brunschwig	CHEM/555A	5, 6			$52,555	$55,000	$55,000	$162,555
01-91	Magnetic Nanodispersions (NANO IV)	L. H. Lewis	MA/480	6			$71,175	$73,000	$77,000	$221,175
01-93	High Resolution Magneto-optical Study of Magnetic Nanostructures, Nanocomposite Functional and Superconducting Materials (NANO IV)	Qiang Li	MA/480	5, 6			$32,748	$46,000	$50,000	$128,748
01-94	Quantum Structure Fabrication and Characterization Using Advanced Transmission Electron Microscopy (NANO IV)	Y. Zhu	ES&T/480	5, 6			$89,486	$0	$0	$89,486
01-97	Ultrafast Power Dependent Dynamics of CdS(Se) Quantum Dots in Glass	D. Imre	Env. Sci./ 815E	5, 7			$87,349	$90,000	$95,000	$272,349
	TOTAL						$5,345,436	$3,498,500	$1,952,100	

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2001 PROJECT PROGRAM SUMMARIES

Performance Enhancement in a Photoinjector Electron Linac

Erik D. Johnson *98-23A*
L. F. DiMauro
W. S. Graves
B. Sheehy
X. Wang

PURPOSE:

Explores previously unmapped parameter space in Photoinjector Electron Linacs with the goal of finding approaches to dramatically improve the performance of this class of machines. There are conflicting theoretical predictions of performance particularly when short and shaped laser pulses are used for driving the photocathode. Some project dramatic enhancement, some marginal improvement, and at present no data exist to sort them out. At a minimum this project represents an experimental investigation to corroborate theory; if successful it provides a proof of principle for a significantly improved performance electron machine.

APPROACH:

In previous supported activities at BNL, the Accelerator Test Facility (ATF) developed an RF photo-cathode gun that was the starting model for our gun (Gun IV). Our gun can be run at higher repetition rate (due to enhanced cooling). To allow better control of the temporal characteristics of the light used to stimulate emission from the cathode, we have developed a laser system using Titanium Sapphire technology, which provides superior bandwidth to allow pulse shaping.

TECHNICAL PROGRESS AND RESULTS:

During FY 2000 we started commissioning of the photo-injector. A photo-beam has been produced and accelerated to the full energy (~200 MeV). Electron bunches of up to 0.3 nC have been accelerated to full energy with normalized emittance of 4 π mm-mrad. During FY2001 we continued with the characterization and optimization of various aspects of the photoinjector operation. While we increased our general knowledge about characterization of the machine, we also made modifications to the gun and the low-level RF system that significantly enhanced the performance.

A modification in the cathode plate was made that separated the function of the vacuum and RF seals. We performed Superfish simulations of the gun field before and after the addition of a gold-plated shorting ring and modification of the cathode plate. The 18% increase in gradient from the simulation results was confirmed by measurement of the electron beam energy. After tuning this had the effect of increasing our gun gradient from 89 MV/m to 105 MV/m without increasing the RF drive power. This is particularly important since increasing the gradient can lead to a reduction in emmittance dilution and a reduction in beam loss due to scraping.

Relatively small but important modifications were made in the low-level RF drive that have substantially improved the phase stability of the electron beam (currently better than 1 ps laser to beam noise). Also made significant progress in improvement of the transverse profile of the UV laser light illuminating the photocathode, which improves the beam quality.

SPECIFIC ACCOMPLISHMENTS:

The following FY2001 publications appear in the proceedings of the 2001 Particle Accelerator Conference: *DUVFEL Photoinjector Dynamics: Measurement and Simulation* by W.S. Graves, D.H. Dowell, R. Heese, E.D. Johnson, J. Rose, T. Shaftan, B. Sheehy, L.-H. Yu.

Ultrashort Electron Bunch Length Measurements at DUVFEL by W.S. Graves, G.L. Carr, D.H. Dowell, A. Doyuran, R. Heese, E.D. Johnson, C. Neuman, J. Rose, T. Shaftan, B. Sheehy.

Measured Properties of the DUVFEL High Brightness, Ultrashort Electron Beam W.S. Graves, D.H. Dowell, A. Doyuran, P. Emma, R. Heese, E.D. Johnson, J. Rose, J. Rudati, T. Shaftan, B. Sheehy, J. Skaritka, L.-H. Yu.

Coherent Radiation Measurements at the NSLS Source Development Lab by G. Lawrence Carr, W.S. Graves, E.D. Johnson, J.B. Murphy C. Neuman.

A recent call from DOD in high energy Free Electron Laser (FEL) systems, prompts the submittal of a proposal to the Office of Naval Research/Joint Technology Office (ONR/JTO) for FY 2002 funding.

LDRD FUNDING:

FY 1999	$300,339
FY 2000	$266,298
FY 2001	$250,429

Pulse Compression and Emittance Preservation in a High Brightness Linac

William S. Graves 98-23B
R. Heese
E. D. Johnson

PURPOSE:

Free electron lasers will obtain substantial performance gains if peak current in electron linacs is increased. This can be achieved by compressing the length of the electron bunch, but it is only beneficial if other properties of the beam, such as emittance, are not degraded. Undesirable emittance growth due to space charge repulsion and the emission of coherent synchrotron radiation (CSR) is expected to limit the maximum peak current. Existing theories vary by more than an order of magnitude on the effect of CSR on emittance. By an experimental study, we can quantify its effect and investigate some of the proposed schemes to mitigate the emittance dilution induced by CSR. If successful, this project will help define the practical limits for the use of pulse compression in advanced machines such as the proposed Photoinjected Energy Recovery Linac (PERL) Project at BNL and the Linac Coherent Light Source (LCLS) X-ray at the Stanford Linear Accelerator Center (SLAC).

APPROACH:

The peak current from a state-of-the-art photoinjector is limited to about 100 A due to space charge effects. We will increase this to as much as 1000 A by compressing the electron bunch after it has been accelerated to high energy.

A four-magnet chicane has been installed at the Deep Ultra-Violet Free Electron Laser (DUVFEL) to compress the beam. The design of this compressor is optimized to reduce CSR emission while producing a short bunch. It has flexibility to alter the bend angle or drift distances between magnets to take advantage of experimental results. It also has the necessary diagnostics, including multiple bunch length measurement instruments and high precision emittance diagnostics, required to measure the effects of CSR on beam emittance.

The bunch length is compressed from approximately 5 ps to 0.5 ps. This process depends sensitively on the phase of the electron beam relative to the accelerating RF field. The phase must be measured and controlled with an accuracy of less than 1 ps. Our design includes instrumentation and controls for this purpose.

TECHNICAL PROGRESS AND RESULTS:

In FY00, the bunch compressor and instrumentation were constructed, and initial beam tests began.

The work in FY01 has focused on studies of the properties of the compressed electron beam and measurement of coherent radiation emitted by the short bunches. Results of the beam studies are summarized in the plots below. The most interesting result to date is the first observation of "microbunching" of the electron beam at high compression. This is the generation of two or more extremely short, distinct high intensity bunches within the original single electron bunch. Following these observations, improved theoretical models now predict that an instability can occur if the initial beam distribution is not smooth in time. Coherent synchrotron radiation from the time-modulations acts on the beam to increase the modulation depth, which in turn increases the radiation emitted, thus creating the instability. In a photoinjector the electron bunch is created by a UV laser pulse striking the copper photocathode. Time modulations on the UV pulse may produce an electron pulse with similar structure. We have succeeded in measuring the time profile of the UV pulse on a timescale of 200 fs and verify

that indeed modulations exist. Detailed comparison of experiment with theory is now underway to test the dependence of the pulse shape on the laser modulation.

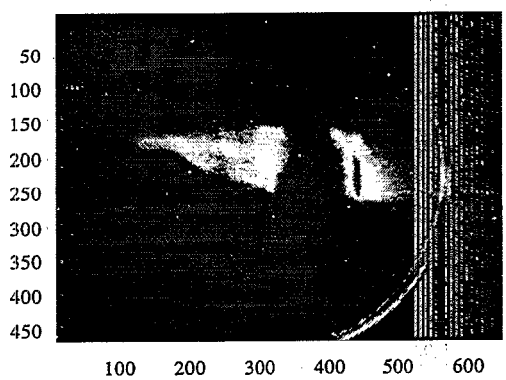


Figure 1: Image from scintillator screen of electron beam stretched in time (horizontal axis). Units are pixels in x and y. Coherent radiation causes beam to separate into distinct bunches.

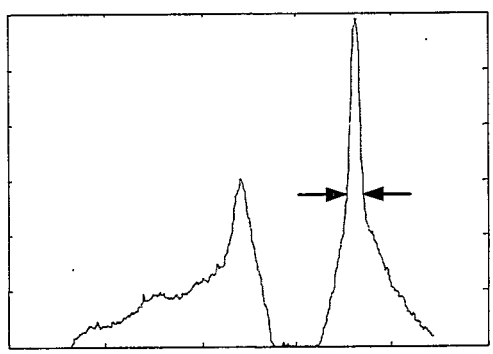


Figure 2: Projection of Fig. 1 onto time axis. Time resolution is ~50 fs.

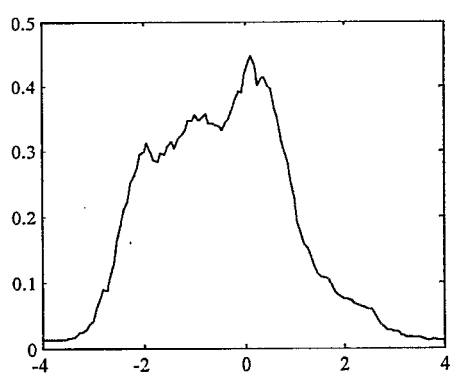


Figure 3: Time profile of UV laser pulse measured by cross-correlation with 100 fs Ti:Sapphire IR pulse. Time resolution is 200 fs. Time structure seeds coherent instability in electron beam.

SPECIFIC ACCOMPLISHMENTS:

In May, 2001 Duke University graduate student, Charles Neuman, completed his PhD thesis for work on the bunch length measurements.

Pre-FY2001 refereed publications are *Coherent Off-Axis Undulator Radiation from Short Electron Bunches* by C.P. Neuman, W.S. Graves, and P.G. O'Shea Phys Rev ST - AB (Mar. 10, 2000) 030701

The following FY2001 publications appear in the proceedings of the 2001 Particle Accelerator Conference: *DUVFEL Photo-injector Dynamics: Measurement and Simulation* by W.S. Graves, D.H. Dowell, R. Heese, E.D. Johnson, J. Rose, T. Shaftan, B. Sheehy, L.-H. Yu. *Ultrashort Electron Bunch Length Measurements at DUVFEL* by W.S. Graves, G.L. Carr, D.H. Dowell, A. Doyuran, R. Heese, E.D. Johnson, C. Neuman, J. Rose, T. Shaftan, B. Sheehy. *Measured Properties of the DUVFEL High Brightness, Ultrashort Electron Beam* by W.S. Graves, D.H. Dowell, A. Doyuran, P. Emma, R. Heese, E.D. Johnson, J. Rose, J. Rudati, T. Shaftan, B. Sheehy, J. Skaritka, L.-H. Yu. *Coherent Radiation Measure-ments at the NSLS Source Development Lab* by G. Lawrence Carr, W.S. Graves, E.D. Johnson, J.B. Murphy, and C. Neuman.

In addition, a manuscript is in preparation for submission to Phys. Rev. describing the microbunching observations. We plan to submit a Field Work Proposal (FWP) to DOE for funding to continue research on the physics of ultrashort electron pulses. These pulses are expected to result in new types of radiation sources with unprecedented intensity over a wide range of wavelengths.

LDRD FUNDING:

FY 1999	$151,621
FY 2000	$133,000
FY 2001	$130,213

Ultra-Fast Detector Based on Optical Techniques

Yannis K. Semertzidis *99-01*

PURPOSE:

A charged particle beam detector based entirely on electro-optical (E-O) techniques is a very promising way to reach time resolution in the range of 10^{-11} s (10ps) to 10^{-14} s (10fs) in a non-destructive way. Efforts are underway at accelerators around the world, including the accelerator test facility (ATF) at BNL, to produce beams with ultra-short bunch lengths and can benefit greatly with the development of this diagnostic technique.

APPROACH:

During the last decade there has been a revolution in sensing ultra-fast electric fields with unprecedented time resolution. Our expertise with optical techniques together with our particle and accelerator physics background helped us marry the two fields. There are 3 collaborating institutes and 10 physicists participating in the effort: V. Castillo, R. Larsen, D.M. Lazarus, D. Nikas, C. Ozben, Y.K. Semertzidis, T. Srinivasan-Rao, and T. Tsang from BNL; L. Kowalski from Montclair State University; and D.E. Kraus from University of Pittsburgh.

The electric field from a relativistic charged particle beam is Lorentz contracted and forms a transverse E-field front. The amplitude of this E-field is proportional to the amount of charge present in the beam. Therefore, a transverse electric field sensor with a good time resolution compared to the time duration of the beam, can reveal the longitudinal profile of the beam. We proposed to use crystals as the transverse E-field sensors by means of the E-O effect.

After we observed the first signals there were still questions about their source. The electric fields present near charged particle beams are very small, and the backgrounds due to wake fields provide significant competition. In order to study this we have constructed an ellipsometer which consists of a polarizer to polarize the laser beam, an electro-optic crystal ($LiNbO_3$), a Quarter Wave Plate (QWP), and an analyzer (i.e. polarizer set in almost full extinction mode). In the absence of an electric field the laser beam going through the crystal is linearly polarized when it enters the crystal and linearly polarized when it exits it. If there is an electric field present near the crystal, then the crystal becomes birefringent and the exiting laser light becomes elliptically polarized for the time the electric field is present. The QWP transforms this ellipticity into a rotation. The analyzer turns the rotation into a time dependent light amplitude modulation. This ellipticity from the $LiNbO_3$ crystal is proportional to the electric field present near the crystal and the E-O effect in this case is called the Pockel's effect. For other materials the induced ellipticity is proportional to the square of the electric field in which case the E-O effect is called the Kerr effect. We have chosen to use the Pockel's effect since it dominates in the small electric field region.

TECHNICAL PROGRESS AND RESULTS:

Our group made the first observation in the world of a charged particle beam by means of the E-O effect. The sensor we used was a commercially available E-O crystal placed near the 10-15ps electron beam available at the ATF of BNL. The total charge per bunch was about 0.6nC and the repetition

rate 1.5Hz. This crystal formed a wave-guide for the laser light, and it was enclosed in a metal case. We had to modify the metal case around the crystal in order to gain beam access to it.

In FY2000, we assembled a system using a bulk crystal ("free space setup") bringing the laser light by means of a fiber all the way from the control room to the beam-line. The laser light came out from the fiber and was coupled into the crystal which was located in the vacuum chamber of the beam-line with the matching optics. After the crystal, the laser light traversed the QWP, and then was coupled to another fiber which carried it to the control room where it was detected by a fast photodiode following the analyzer. The output of the amplifier was connected to a fast oscilloscope.

We again observed the signal in the presence of the charged particle beam. The observed rise-time of the signal was 70ps limited by the bandwidth of the oscilloscope. In a series of tests we checked the polarity dependence of the signal when the beam was above versus below the crystal. The electric field sensed by the crystal changes polarity and so did the signal. We also rotated the laser polarization vector by 90 degrees and again the signal polarity flipped sign as expected. Due to the Lorentz contraction and the finite speed of light, the signal dependence is inversely proportional to the distance from the crystal. The 1/r dependence was confirmed in a series of measurements.

This method is fully utilized when all parts of the system have very high bandwidth, and there are no slow components in it. One way to achieve this is to use only components based on E-O effects. In place of the charge pre-amplifier we will use (in the next step) a streak camera capable of bringing the time resolution to below 10ps. In the laboratory we have tested the operation mode of a streak camera available to us, and we were able to achieve the above time resolution with a low energy pulsed laser in the presence of a Continuous Wave (CW) laser used to simulate the background. In FY2001, we will achieve the signal detection using electric fields between parallel plates. The output of this setup is coupled to a streak camera which has a time resolution of 2-10ps. After this is achieved we will run at the ATF with the electron beam providing the electric field near the crystal.

After this program is completed we will use Frequency Resolved Optical Gating (FROG) techniques or new techniques developed by our group to achieve sub-ps time resolution in single shot. We are currently seeking funding from DOE for the application of FROG or our new techniques.

SPECIFIC ACCOMPLISHMENTS:

We are in the process of applying for a patent on our method of achieving sub-ps time resolution.

We have made the following presentations (with proceedings available):
Y. Semertzidis, et al., Particle Accelerator Conference, NY, March 29, 1999.
D. Lazarus et al., International Europhysics Conference-HEP99, Tampere, Finland, 1999.
D. Nikas, et al., DPF2000, Columbus Ohio, August, 2000.
We published the article (refereed): Y.K. Semertzidis, et al., NIMA 396, 452, 2000.
Submitted the following article (refereed): T. Tsang, et al., JAP.

LDRD FUNDING:

FY 1999	$113,345
FY 2000	$ 88,932
FY 2001	$ 80,000

Efficacy of Unidirectional Microbeam Radiation Therapy in Treating Malignant Tumors: Preclinical Studies in Rats and Mice

F. Avraham Dilmanian *99-41*
G.M. Morris, T. Bacarian, M.E. Berens, A. Fuchs, J.F. Hainfeld, J. Kalef-Ezra, J.S. Laterra, S. Packer, L.A. Peña, B. Ren, J.K. Robinson, E.M. Rosen, J. Tammam, R. Yakupov, and N. Zhong

PURPOSE:

The goals of this LDRD have been to use animal models to: a) determine the irradiation parameters that optimize the microbeam radiation therapy (MRT) effects of sparing of normal tissues and preferentially killing tumors, b) find the dose limits for the normal-tissue sparing of microbeams on the central nervous system, the eye, and the skin, c) obtain the therapeutic index (maximum dose tolerated by the normal tissue divided by the dose needed for tumor ablation) of MRT vs. broad beams for the highly malignant tumors of intracranial rat 9L gliosarcoma (9LGS) and subcutaneous murine EMT-6 carcinoma, d) investigate the biological mechanisms underlying the MRT effects.

APPROACH:

MRT is a novel experimental method that was originated at the National Synchrotron Light Source (NSLS) in the early 1990s. It uses arrays of parallel, thin (<100 μm) planes of synchrotron-generated x rays (microplanar beams, microbeams). MRT is commonly administered in a single exposure, as opposed to 30-50 daily dose fractions used in conventional radiotherapy. The high risk related to MRT research is that, like any other preclinical work, its clinical efficacy can be determined only by human studies, although animal studies help to address potential problems. Animal studies can provide proof of concept of feasibility as evident from the results presented in this report. The experiments were carried out at the X17B1 superconducting beamline of the NSLS. The microplanar beams in the arrays have been 27- to 90-μm wide and up to several centimeters long, spaced 50- to 300-μm center-to-center, with a median beam energy of 65 to 120 keV. They were oriented either horizontally or vertically.

TECHNICAL PROGRESS AND RESULTS:

The FY00 progress included preliminary results on the tolerance to MRT of the spinal cord, skin, and eye, as well as response to MRT of the 9LGS and EMT-6 tumors. This report includes results of newly acquired data on the rat skin, the EMT-6 tumors, and mechanistic studies, together with advanced data analysis of the results reported in FY00.

Studies With Normal Tissues

i. Radiation tolerance of rat spinal cord:
Rats were irradiated laterally in their cervical spinal cord with single-fraction microbeams and broad beams at 7-mm length of the irradiated field. The end points were paralysis and occult neurological effects observed in the behavioral method of Rotor-rod that tests sensori-motor effects. The observations continued for one year after irradiations. Very large in-beam microbeam doses (600 Gy) were tolerated by the spinal cord without evidence of neurological or behavioral impairments, whereas 50 Gy broad-beam dose resulted in paralysis, and 25 Gy broad-beam dose lead to neurological deficits seen by Rotor-rod tests.

ii. Radiation tolerance of the normal rabbit eye

Rabbit eyes were irradiated with microbeams (27-μm width, 100-μm spacing) or broad beams in groups of two rabbits. No damage to the retina or cornea was observed in the eye exams, or histologically, at 312 Gy in-beam microbeam dose within year after irradiations, and the damage from 625 Gy microbeams was slight and limited to one rabbit; the damage from 156 Gy broad beams was severe.

iii. Radiation tolerance of the normal rat skin

Rat skin was irradiated with unidirectional microbeams, using 90 μm beam width, 300 μm beam spacing, and 120 keV median spectral energy. The biological end point was moist desquamation caused by the breakdown of the surface layer (epidermis) of the skin. This effect was shallower and more transient for microbeams compared to that from broad beams. Eight groups of rats (6 per group) were irradiated at skin doses ranging from 820 to 1150 Gy in-beam skin doses. The ED_{50} (50% endpoint dose) is approximately about 980 Gy in-beam dose. Our broad beams have been incomplete and do not allow the ED_{50} calculation for moist desquamation, although it appears to be not far above 40 Gy. Therefore, the tolerance advantage of microbeams over broad beams is at least 20-fold, 6-fold when integrated microbeam doses are used. We conclude that MRT's net tolerance advantage over conventional beams is much larger than its disadvantage in giving higher skin dose to the subject (because of its lower beam energy), which is about 3-fold for 10-cm tissue depth.

Studies With Animal Tumor Models:

i. Intracerebral 9LGS rat brain tumors

Rats with intracranial 9LGS tumors were exposed laterally using a single microbeam 27 μm wide and 3.8 mm-high stepwise to produce irradiation arrays with 50, 75, or 100 μm on-center beam spacings and 150, 250, 300, or 500 Gy in-slice, skin-entrance, single-exposure doses. When all data were collated, the median survival was 70 days; no depletion of nerve cells was observed. However, when data from the highest skin-entrance dose and/or the smallest microbeam spacings were excluded, the median survival time of the subset of the rats was 170 days, and no white matter necrosis was observed. Others have reported unilateral single-exposure broad-beam irradiation of the intracranial 9LGS at 22.5 Gy with a median survival of only ~34 days and with severe depletion of neurons. These results suggest that the therapeutic index of unidirectional microbeams is larger than that of the broad beams, and that MRT may later find applications in treating certain malignant brain tumors (*Neuro-Oncology*, in press).

ii. Subcutaneous murine carcinoma EMT-6

Subcutaneous EMT6 mouse mammary tumor model was used to compare the therapeutic efficacy of single-fraction, unidirectional irradiation by: 1) MRT, using co-planar microbeams; 2) MRT, using cross-planar microbeams (*i.e.*, vertical and horizontal microbeams from the same angle); and 3) conventional broad beams from the same synchrotron source. At doses of radiation that eradicated 75-85% of the tumors (650 Gy microbeams, 45 Gy broad beams), the rates of acute normal tissue toxicity (moist desquamation and epilation) and delayed toxicity (leg swelling and failure of hair regrowth) were significantly lower in the cross-planar microbeams as compared with broad beams. These findings suggest that microbeams can produce high rates of tumor control with relatively little toxicity. (Yamagata Proceedings, in press).

Mechanistic Studies:

i. BrdU experiment

The role of endothelial cell proliferation in tissue recovery from microbeams was examined in the rat cerebellum using a marker for cell division, bromodeoxyuridine (BrdU). Rats were irradiated with vertical microbeams of 80 μm beam width and 400 μm spacing at 200 Gy in-beam entrance dose. The animals were injected with BrdU before they were euthanized for histology at 1, 1.5, 2, 2.5, 3, 3.5, and 4 days after the irradiation. Tissue sections were stained both with anti-BrdU and lectin (to label endothelial cells). The increase in the number of proliferating endothelial cells from day 1 to days 4 was significant. The results may indicate that microbeams initiated a process of cell proliferation that accelerated during the period of the measurements, but probably did not reach its peak.

ii. Neuronal cell death in the rat cerebellum.

Rats were irradiated in their cerebellum using a microbeam 27 μm wide, spaced 200 μm apart, in a repetitive dose pattern of 1200, 500, 400, 300, 200, 1200, 200, 300, 400, 500 Gy. The rats were perfused/euthanized in the following time points: 0.5 d, 1 d, 2 d, 7 d, 14 d, 30 d, and 60 d, and the tissue was stained with hematoxylin and eosin (H & E). The results indicated that clear stripes of neuronal cell loss were observable at the 1200 and 500 Gy starting two days after the irradiations. These findings enable us to demarcate paths of microbeams on the histology slides for biological MRT studies two days after irradiations using high microbeam doses.

SPECIFIC ACCOMPLISHMENTS:

Publications

F.A. Dilmanian, et al. Response of avian embryonic brain to spatially segmented x-ray microbeams. Cellular and Molecular Biology 47: 485-493, 2001.

F.A. Dilmanian, et al. Response of rat intracranial 9L gliosarcoma to microbeams radiation therapy. Neuro-Oncology, in press.

F.A. Dilmanian, et al. Response of Subcutaneous Murine Mammary Carcinoma EMT-6 to Synchrotron-generated Segmented X-ray Microbeams," Proceedings of the Joint Symposium on Bio-Sensing and Bio-Imaging," August 2-4, 2001, Yamagata, Japan, in press.

F.A. Dilmanian, et al. Improved therapeutic efficacy of microbeam radiation therapy (MRT) for experimental carcinoma tumors. (being submitted to Cancer Research)

Eight abstracts were published in the Annual Activity Reports 2000 and 2001 of the NSLS, including the following:

F.A. Dilmanian, et al. Design of a dedicated medical synchrotron x-ray facility primarily for Microbeam Radiation Therapy (MRT). NSLS Activity Report 2001.

Patent Application (pending)

F.A. Dilmanian and G.M. Morris. Methods for Implementing Microbeam Radiation Therapy in Patient Treatment. Record of Invention submitted to the BNL Office of Technology Transfer, August 25, 2000.

Grant Applications

A grant proposal submitted to the OBER, U.S. DOE, was reviewed favorably. A small amount of funds was already granted to us for FY 02, and the grant is being considered for further funding.

An NIH R01 proposal, submitted on February 16, 2001, received a fair but not fundable score. It was amended and resubmitted on November 1, 2001.

An NIH R21 proposal, submitted on June 1, 2001, received a fair but not fundable score. It is being amended for resubmission on March 1, 2002.

LDRD FUNDING:

FY 1999	$119,571
FY 2000	$149,204
FY 2001	$127,877

Experimental and Theoretical Investigations of Transition Metal Oxides

John P. Hill *99-46*
D. Gibbs

PURPOSE:

The purpose of this project was to push forward the development of new resonant x-ray scattering techniques in the study of transition metal oxides. These materials are interesting from both a fundamental and applied perspective. The new x-ray techniques shed light on the charge and orbital degrees of freedom which play a central role in determining the materials' properties.

APPROACH:

Work began in the manganite systems, to gain insight into both the systems themselves and the technique. The next goal was to extend the application of the technique beyond the manganites to other transition metal oxides.

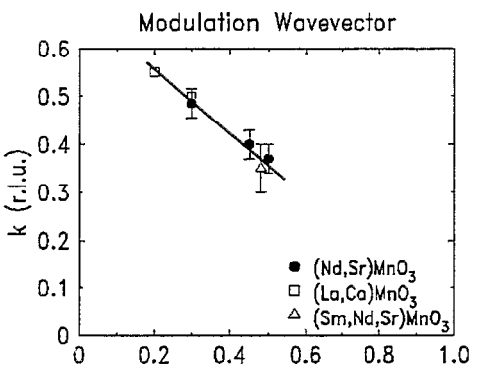
Collaborators include Y. Murakmai (K.E.K.), V. Kiryukhin and S.-W. Cheong (Rutgers U.), B. Keimer (MPI-Stuttgart), and Y. Tokura (U. Tokyo).

TECHNICAL PROGRESS AND RESULTS:

In FY00, an investigation was begun into the high temperature correlations in two different manganites, $Pr_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$. It was discovered that each exhibit similar structural correlations with the same wave-vector and correlation length. This work pointed to the robust nature of such correlations and hinted at their importance.

In FY01, this work was continued and extended to a third manganite $Nd_{1-x}Sr_xMnO_3$. Again similar correlations were observed. In this system the doping and field dependence was investigated. Remarkably, we find that the wave-vector varies linearly with x; a result that has yet to be explained (Fig. 1). Subsequent investigation of other systems show that they also fall on the same curve.

Further, experiments performed in an applied magnetic field reveal that these correlations are greatly reduced at the metal-insulator transition - in contrast to the uncorrelated distortions that we also observe. Thus, it appears that these structural correlations are intimately connected with the field-driven metal-insulator transition and consequently with the colossal magnetoresistance effect in these materials.



This was the final year of this LDRD. The work will continue in the future funded by a successful proposal to the DOE on charge inhomogeneities in strongly correlated systems. This grant currently supports two post-docs on LDRD-related work. Their present focus includes electronic excitations in transition metal oxides and charge and orbital ordering in thin films.

SPECIFIC ACCOMPLISHMENTS:

Invited talks

1. American Physical Society, Seattle (March, 2001)

2. Plenary Talk, International Conference on Magnetic Materials, Calcutta (Oct. 2000).\
3. Plenary Talk, XRMS 2000, Frei Universitat Berlin, Germany, December 2000.
4. CMMP 2000, Bristol, U.K., December 2000.
5. Boston University, December, 2000.
6. Materials Research Society, San Francisco, April 2001.
7. International Workshop on Inelastic X-ray Scattering, IXS 2001, Helsinki, Finland, August 2001.
8. International Conference on Strongly Correlated Electrons with Orbital Degrees of Freedom, Orbital 2001, Sendai, Japan, September 2001.

Publications

1. Casa. D. et al. Phys. Rev. B: Rapid Commun. 64, 100404-1—100404-4 (2001).
2. Gibbs, D., et al, *in: Third Generation Hard X-ray Synchrotron Radiation Sources: Source Properties, Optics and Experimental Techniques*, D. Mills, Editor, J. Wiley & Sons, Publisher (in press).
3. Gibbs, D. Synchrotron Radiation News (in press).
4. Hill, J.P., et al, Appl. Phys. A (in press).
5. Hill, J.P. *in: Methods in Materials Research*, John Wiley & Sons.
6. Hill, J. Synchrotron Radiation News (in press).
7. Keimer, B., et al, Phys. Rev. Lett. 85(18), 3946-3949 (2000).
8. Kiryukhin, V., et al, Phys. Rev. B 63, 024420 (2000).
9. Kiryukhim, et al, Phys. Rev. B 63, 144406 (2001).
10. Kiryukhin, et al, Phys. Rev. B (submitted)
11. Kiryukhin, V., et al, Phys. Rev. Lett. (submitted)
12. Nakao, H. et al, Phys. Rev. Lett. 85, 4349-53 (2000).
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14. Nelson, C.S., et al, . Phys. Rev. B 64, 174405 (2001).
15. Nelson, C.S., et al, In: Vibronic Interactions: Jahn-Teller Effect in Crystals and Molecules, edited by M.D. Kaplan and G.O. Zimmerman, Kluwer Academic Publishers, Dordrecht, 2001.
16. Nelson, C.S., et al, Mat. Res. Soc. Symp. Proc. 678 (in press).
17. Nelson, C.S., et al, In: Manganites and Other Compounds, Elbio Dagotto (Editor), Springer-Verlag, Publisher, 2001 (submitted).
18. Murakami, Y., et al, in Vol. 590, "Application of Synchrotron Radiation Techniques to Materials Science V," S.R. Stock, D.L. Perry, and S.M. Mini, Eds., ISBN: 1-55899-498-X (in press).
19. von Zimmermann, et al, J. Magn. Magn. Mat. 233, 31-37 (2001).
20. von Zimmermann, et al, Phys. Rev. B 64, 064411-064411-9 (2001).
21. von Zimmermann, et al, in $Pr_{1-x}Ca_xMnO_3$. Phys. Rev. B (in press).
22. Zaliznyak, I.A., et al, Phys. Rev. Lett. 85, 3946 (2000).

Supported Researchers

1 Post-doc (M. von Zimmermann)
Travel to various facilities for experiments, including the Advanced Photon Source and the European Synchrotron Radiation Facility. Travel to selected meetings.

Note: During FY01, M. von Zimmermann obtained a permanent position at HASYLAB, Germany.

LDRD FUNDING:

FY 1999	$84,381
FY 2000	$61,969
FY 2001	$58,474

High Gain FEL Amplifier

George Rakowsky *99-51A*
W. S. Graves
E. D. Johnson

PURPOSE:

For High Gain Free Electron Lasers (FELs) to work as single pass devices at short wavelengths, very long wigglers are required for the amplifier. These devices would (in principle) be most efficient if they can be built without gaps for diagnostics and trajectory correction magnets. The aim of this project is to demonstrate the approach experimentally.

APPROACH:

As a starting point, we obtained the 10-meter long Near Infra-red Scaleable Undulator System (NISUS) wiggler (from a canceled Army program) to use for this proof of principle experiment. The objective is to see if it can be measured and shimmed to the tolerances required for an FEL amplifier and to demonstrate the viability of the long seamless wiggler design approach. The measured data will be used as input to model an FEL amplifier, which will help establish realistic expectations for FEL performance.

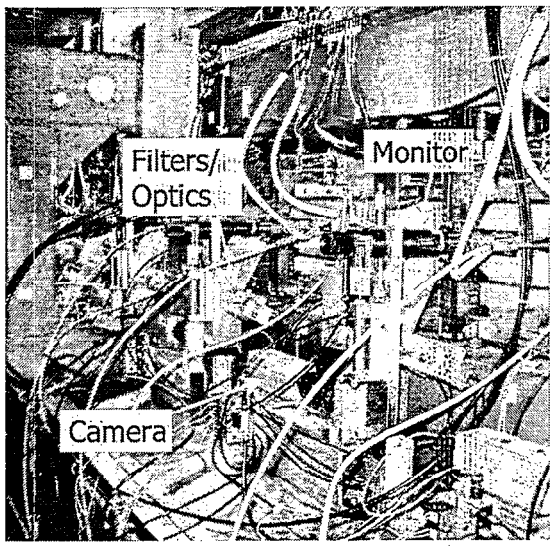
TECHNICAL PROGRESS AND RESULTS:

In FY 1999, we contracted with STI Optronics of Bellevue, WA, the company that designed and built NISUS for Boeing, to assist in the mapping of the magnetic field. STI's 3-meter long magnetic field mapper was modified to fit the tight confines of the NISUS geometry, and the full 10-meter device was measured in four overlapping scans along the magnetic axis.

The initial magnetic field mapping was completed in early FY 2000, at a gap of 14.4 mm. The cumulative effect of field errors results in a large walk-off from the magnetic axis, which would have even exceeded the aperture of the vacuum beampipe. In effect, the beam would have hit the wall.

For the shimming operation, the final gap was set to 20.6 mm, to achieve a peak undulator field of 0.31 Tesla, for resonance at 400 nm with an electron beam energy of 144 MeV. To straighten the trajectory, STI applied shaped steel shims of various thicknesses to appropriate undulator poles, according to a proprietary algorithm. The field was remapped, the trajectory recalculated and the shimming process was iterated as necessary to reduce trajectory wander to less than a "wiggle amplitude" (approximately 25 μm) over each 3-meter scan length. Corrections were made in the local gaps to achieve a final rms phase error of only 4°, well within our requirements.

In FY 2001, with the NISUS magnet shimmed and fully characterized, the vacuum chamber was assembled and installed. The electrical connections to the 4-wire steering system completed the optical diagnostic system. A pop-in diagnostic monitor system was developed and installed that allows the characterization of the electron beam trajectory at each segment of the undulator. A novel two-station monitor was developed that has Ce:YAG scintillator screens to monitor electron beam positions, and a mirror to extract light from the FEL on the second station. Late in the year, electron beams successfully traversed the undulator. Steering corrections were larger than anticipated. Examination of this problem is continuing under funding provided by a grant from the Air Force Office of Scientific Research.



Monitors in place on NISUS. The monitor actuator and camera are shown for one monitor, the arrow to the optics and filters points to the next monitor down beam. 17 such monitoring stations are located on the NISUS undulator to provide detailed information about the electron beam position and beam properties.

SPECIFIC ACCOMPLISHMENTS:

The following FY2001 publication appears in the proceedings of the 2001 Particle Accelerator Conference, several others related to other aspects of the DUV-FEL were presented:

Measured Properties of the DUVFEL High Brightness, Ultrashort Electron Beam

W.S. Graves, D.H. Dowell, A. Doyuran, P. Emma, R. Heese, E.D. Johnson, J. Rose, J. Rudati, T. Shaftan, B. Sheehy, J. Skaritka, L.-H. Yu.

Also in FY2001, a research grant entitled "Short Wavelength High Gain Harmonic Generation Free Electron Laser" was funded by AFOSR based in part on this work. The initial funding for the project is $400K.

LDRD FUNDING:

FY 1999	$372,668
FY 2000	$100,000
FY 2001	$182,871

Deep Ultra-Violet Free-Electron Laser Optimization

Erik D. Johnson *99-51B*
W. S. Graves
B. Sheehy
L. H. Yu

PURPOSE:

Free Electron Lasers (FELs) represent the frontier in accelerator based light sources. While there are many theoretical studies, there are relatively few experiments at short wavelength. None have yet monitored the FEL process as the photon and electron beams propagate through a continuous amplifier. This is especially important if tapering is to be used to provide energy extraction beyond FEL saturation. This project examines these issues experimentally and will provide data that can be used to qualify models for projecting the performance of future light sources.

APPROACH:

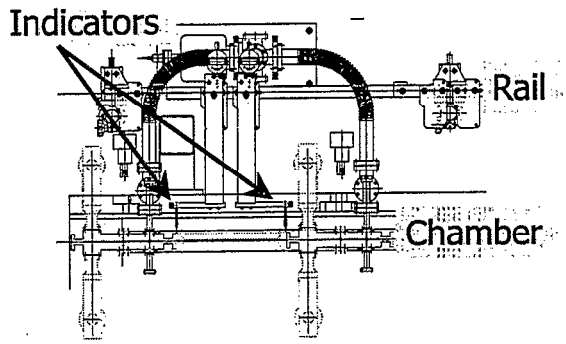
A critical element of the Deep Ultra-Violet Free-Electron Laser (DUV-FEL) project is the optical amplifier. This requires a long magnetic undulator, electron beam diagnostics and controls, and an optical system to collect the light from the FEL and preserve its coherence as it is delivered to the experimental station.

The US Army has transferred ownership of the Near Infra-red Scaleable Undulator System (NISUS) undulator to BNL. This 10-meter long undulator is very flexible, and can be used to explore the way in which electron beam parameters influence FEL output. The vacuum system and diagnostics will be developed and assembled in the existing undulator. Light from the FEL will be relayed out to an optical table with a simple first surface mirror transport line. Initial experiments will be conducted in the visible due to the ready availability and high quality of optical diagnostics.

TECHNICAL PROGRESS AND RESULTS:

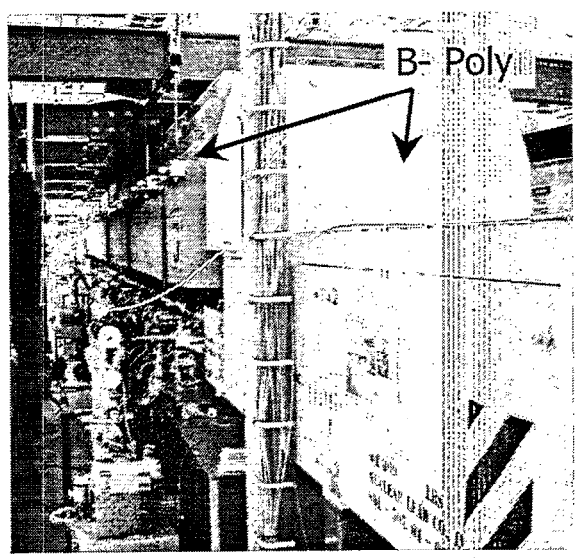
NISUS was built in 16 segments, each with its own four-wire steering section built into the vacuum chamber. Each section also has a port for a diagnostic probe to be inserted to measure the position and profile of the electron beam. Extensive thermal and vacuum cycling stability tests of the undulator vacuum system have shown a tendency of the chamber to creep by as much as 250 microns. The chamber carries the steering/corrector magnets with it when it moves. Motions of these magnets must be at or below the 30-micron level to assure an adequately straight trajectory of the electron beam through the wiggler.

In FY 2001 we developed, tested, and implemented a multi-pronged approach to solving the precision alignment problem. One branch of the alignment system uses a tracking laser that can be observed within the pop-in monitors. The other independent means of alignment is a parallel mechanical rail system with precision offset measuring tools. With these two alignment tools in place, we have positioned the chamber and monitors to a precision of better than fifty microns. The final stage of alignment utilizes the electron beam launched through the undulator illuminating the same pop-in monitors that are used in the laser alignment. Comparison of the trajectory with the laser beam reduces the uncertainty of the beam position to less than 30 microns.



Plan view of the alignment rail and NISUS vacuum chamber. The indicators measured the offset from the rail to the corrector magnets.

This plan requires extensive use of the monitors, which represent significant electron loss points in the accelerator when they are inserted during operation.



Photograph of installed shielding. The borated polyethylene is on tracks and can be rolled away from the undulator to facilitate work on the diagnostics.

A shielding design study undertaken in FY2000 resulted in the shielding built and installed in FY2001 to allow safe operation of the DUV-FEL along with comparatively simple access to work on the complex undulator system.

The undulator magnet materials turn out to provide adequate x-ray shielding in the vertical direction, but additional shielding is required for x-rays that scatter to the sides. To minimize loading on the table, form fitting lead shielding was designed that is precast in small sections. The shielding allows for the required penetrations for diagnostics with the smallest possible opening. Initial trajectory measurements late in the year demonstrated the validity of the approach, although further work will be required to refine the trajectory.

SPECIFIC ACCOMPLISHMENTS:

This work was presented at the Workshop on "Free-Electron Laser Development for Naval Applications" June 6, 2001, in Newport News, VA, "DUV-FEL Current Status and Developments" E.D. Johnson.

Also in FY2001, a research grant entitled "Short Wavelength High Gain Harmonic Generation Free-Electron Laser" was funded by AFOSR based in part on this work. The initial funding for the project is $400K.

LDRD FUNDING:

FY 1999	$124,222
FY 2000	$298,107
FY 2001	$180,742

Development of High-Brightness Electron Sources

Ilan Ben-Zvi *99-53*

PURPOSE:

The objective of this work is to develop brighter electron beams from photoinjector electron sources. This is done through the development of innovative electron beam diagnostics and photoinjectors. Getting a higher brightness in electron beams is cutting edge R&D with high risks of not getting an improvement, but the payoff could be high in enabling new radiation sources such as x-ray Free Electron Lasers (FELs) and Photoinjected Energy Recovery Linacs (PERL).

APPROACH:

The PI, in collaboration with other members of the BNL Accelerator Test Facility (ATF) staff (in particular X.J. Wang, V. Yakimenko, M. Babzien and R. Malone, and research collaborators X.Y. Chang, F. Zhou and S. Kashiwagi) undertook to carry out a series of diagnostic development, precision measurements of the ATF's photoinjector and other issues related to the preservation of beam brightness in linear accelerator systems. The results have been outstanding both in the record brightness achieved and in the measurements of critical phenomena related to the generation and preservation of high-brightness electron beams.

TECHNICAL PROGRESS AND RESULTS:

In FY 1999, we made progress on beam transport analysis and control, RF phase control, Mathcad-based tomography software, electron-beam orbit correction and photoinjector numerical simulations, as described in detail in the 1999 report.

In FY 2000, we made progress on the following subjects:
1. Design Studies of a 120 Hz high-brightness RF Gun for the LCLS.
2. Photoelectron Beam Longitudinal Phase Space reconstruction using Tomography Techniques.
3. Photoelectron Beam Dynamics Studies.
4. Tomographic measurement of the transverse phase space distribution of three longitudinal slices of a beam.

Progress in FY 2001:

1. High Brightness: An emittance of 0.8 mm normalized RMS was measured for a 0.5 nC / 60 MeV electron beam. This is a brightness world record for this class of beams. The steps that were taken to achieve this result were:

a. The stability of the photocathode laser and RF system were improved.
b. A beam based alignment method was developed and implemented for the focusing quads to transport the beam through the linac's center.
c. The accelerating gradient in the RF GUN was increased to ~110 MV/m.
d. The laser spot on the cathode was optimized to generate a round beam.
e. Damaged optical lens in the laser transport was identified & replaced.
f. The beam was tuned to maximize gain in the VISA FEL.

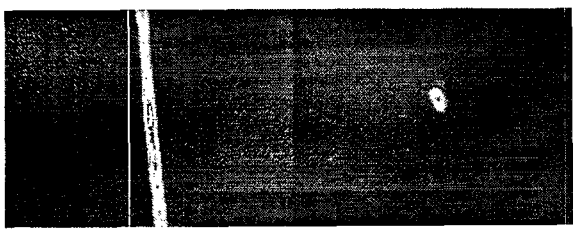


Figure 1. ATF beam spot compared to a 30 micron diameter wire.

A nice visual representation of the beam quality can be seen in Figure 1 which shows the beam size (right) compared to a 30 micron wire (left).

2. PERL Photo-injector Studies: Extensive studies were made on the various options for the PERL injector. The L-band photo-cathode has an advantage over DC gun and 430 MHz photocathode in both beam quality performance and emittance preservation during acceleration and compression.

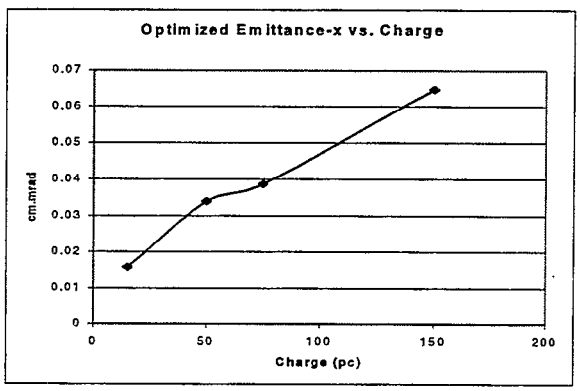


Figure 2. Transverse emittance vs. charge for 2.6 cell RF gun.

Figure 2 shows the transverse emittance as function of charge for a 2.6 cell L-band RF gun operating at a field of 15 MV/m. Emittance less than 1 mm-mrad is expected for a 150 pC charge. We also investigated longitudinal electron beam phase space

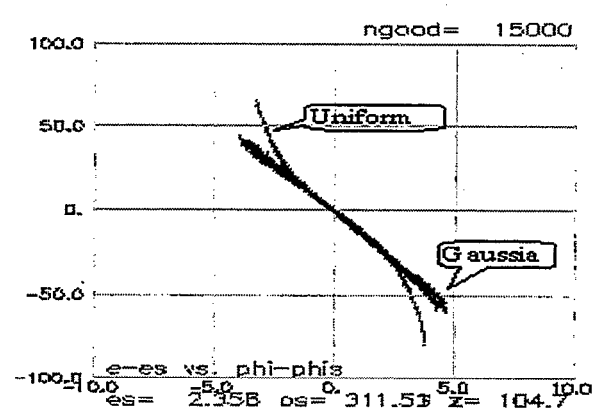


Figure 3. Photoelectron beam longitudinal phase space distribution.

distribution for various laser pulse shapes (Fig. 3). This is critical for ultra-short bunch production. This study revealed that, even though a uniform laser pulse has a small local energy spread, it has a larger nonlinearity compared to Gaussian laser pulse. This is an unexpected result.

3. Experimental Study of Surface Roughness Wakefield: Surface roughness wakefield is an important emittance dilution mechanism in x-ray FELs and PERLs. Our ATF experiment used three beam pipes with artificial bumps mimicking the surface roughness. The measurement results cannot be explained only with purely inductive impedance, since the energy loss and additional energy spread are observed. It hints that an isolated synchronous mode may exist in the beam pipe. A single frequency for the synchronous mode is fitted well with the measurements for both the energy spread and energy loss as shown in Figures 4-6. Furthermore, the dielectric constant, ε, used in the dielectric layer model to calculate the synchronous frequencies of our pipes is 1.3, which is comparable with 1.5 in the dielectric layer model. The preliminary analysis shows that the surface roughness wakefield effects come from both a pure inductive impedance and a resistive part produced by an isolated synchronous mode.

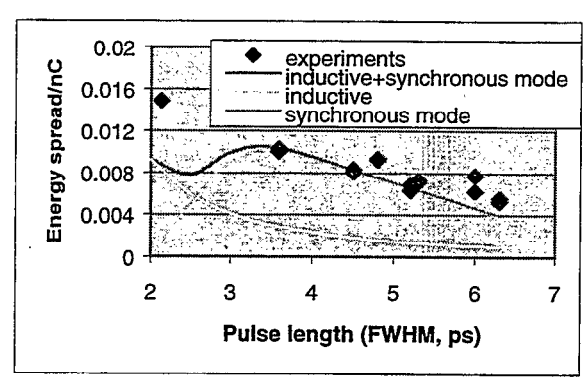


Figure 4. Energy spread (per nC) vs. bunch length (ps) for pipe with small bumps.

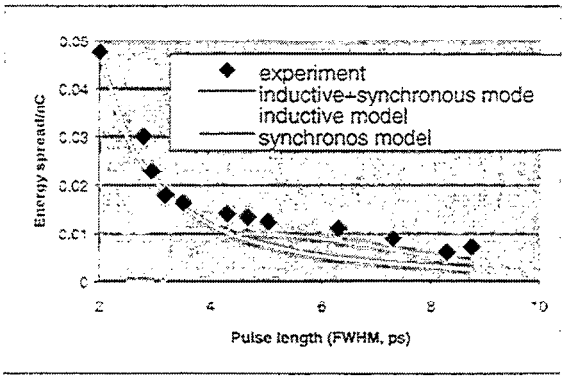


Figure 5. Energy spread (per nC) vs. bunch length for pipe with large bumps.

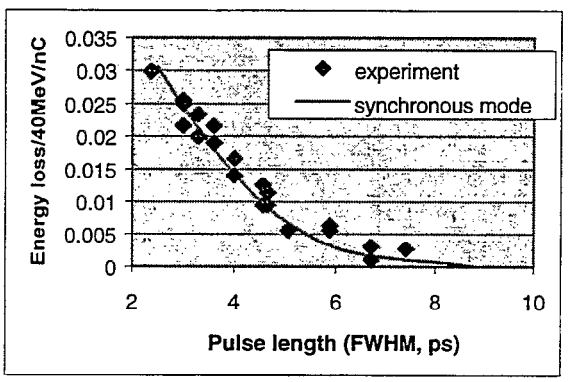


Figure 6. Energy loss (per nC) vs. bunch length (ps) for pipe with large bumps.

4. Transverse Emittance vs. Laser Uniformity: Laser distribution on the cathode is critical for the electron beam performance in a photoinjector. A non-uniform laser produces non-uniform electron beams, which gives rise to non-linear space charge forces that lead to emittance growth. We created cylindrically symmetric, artificial laser transverse distributions on the cathode, and the electron beam emittances were measured at the ATF for a bunch charge of 0.5 nC. The measured transverse emittances are compared with the PARMELA simulations. The simulations and measurements are in good agreement. For one (most non-uniform) laser profile, the emittance as a function of the bunch charge was measured, and these measurements are also in good agreement, except that PARMELA seems to overestimate the emittance when it is very small.

SPECIFIC ACCOMPLISHMENTS:

X. Wang, Progress And Future Directions in High-Brightness Electron Beam Sources, Proceedings, 2001 Particle Accelerator Conference, Chicago IL. June 18-22, 2001.

X.J. Wang, et al, High-Rep Rate Photocathode Injector for LCLS, Proceedings, 2001 Particle Accelerator Conference, Chicago IL. June 18-22, 2001.

A. Murokh, et al, Limitations On Measuring a Transverse Profile of Ultra-Dense Electron Beams with Scintillators, Proceedings, 2001 Particle Accelerator Conference, Chicago IL. June 18-22, 2001.

X.Y. Chang, X.J. Wang, I. Ben-Zvi, BNL Photo-Injector Performance Optimization, Proceedings, 2001 Particle Accelerator Conference, Chicago IL. June 18-22, 2001.

X.J. Wang, et al, Critical Issues in Photo-injector Performance. Proceedings, 2001 International FEL Conference, Darmstadt Germany, August 20-24, 2001.

X.J. Wang et al, Schottky Effect and Mg Cathode Studies at the ATF, Proceedings, 2001 International FEL Conference, Darmstadt Germany, August 20-24, 2001.

V. Yakimenko, et al, Submicron emittance and ultra small beam size measurements at ATF. Proceedings, 2001 International FEL Conference, Darmstadt Germany, August 20-24, 2001.

LDRD FUNDING:

FY 1999	$201,393
FY 2000	$199,807
FY 2001	$ 98,349

Attosecond Pulse Generation in High Harmonics

Louis F. DiMauro *99-56*
B. Sheehy

PURPOSE:

The experimental realization of light pulses with attosecond time duration (10^{-18} seconds) would represent a new frontier in optical science and open new areas of research. The scientific interest encompasses atomic physics, femtosecond chemistry, and material science. The extreme bandwidth requirement of an attosecond light pulse renders conventional laser materials useless. One novel approach to this problem is the use of an extreme nonlinear process to generate a frequency comb of high harmonic radiation. In principle, the comb can extend from the ultraviolet to the soft x-rays providing ample bandwidth for attosecond pulses. The key for achieving temporal compression depends upon the phase relationship between the electric fields of the harmonic comb. The objective is to exploit the use of nonlinear processes for both the formation and measurement of attosecond pulses.

APPROACH:

An intense mid-infrared (3-5 μm) atomic excitation is used to produce high harmonic radiation in a spectral (visible/near-UV) region accessible to common optical materials and well-established optical characterization methods, e.g. frequency-resolved optical gating (FROG). Theory suggests that the formation of attosecond pulses using high harmonic radiation is possible. Previous studies have established the correct physical scaling of the interaction of an intense laser with an alkali metal atom used in these experiments. Accurate measurements of the harmonic light can unequivocally establish whether an attosecond pulse can be formed and will serve as an important check in navigating the experimental difficulties involved in maintaining, measuring, and using such pulses in real experiments. Attosecond pulses are extremely fragile, and our spectral measurements will tell whether the field and phase relationships necessary for the formation of the pulse exist, independent of the experimental complications that might cause the pulse to disperse before it reached the target.

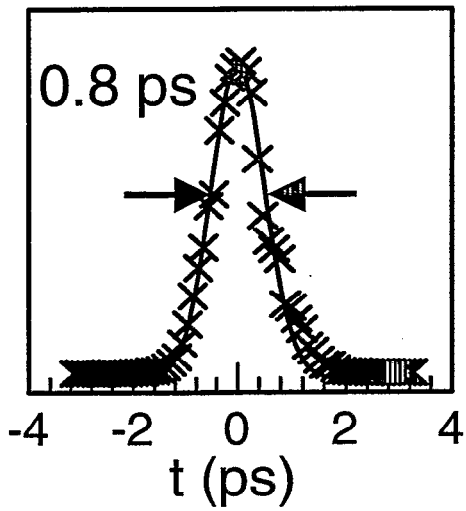
These studies have been the work of Mr. Todd Clatterbuck (a SUNY Stony Brook physics graduate student) and a post-doctoral research associate, Dr. Claire Lynga.

TECHNICAL PROGRESS AND RESULTS:

In FY1999. we established the fundamental principles of our approach. High harmonics were produced from an alkali atom interacting with a long wavelength ($\lambda > 3$ μm) fundamental laser. The high harmonics produced in this manner emit in the visible/near-ultraviolet region of the electromagnetic spectrum. Thus, well-established techniques can be applied to measure the harmonics amplitude and phase.

In FY2000, we overcame many of the significant technical barriers for accomplishing the proposed science. We demonstrated the ability to generate a large enough number of harmonic photons to drive a nonlinear process and recorded the first autocorrelation temporal measurement of high harmonic radiation. *Autocorrelation and all the advanced optical metrology necessary to measure the relevant information for ultra-short pulses rely on a nonlinear interaction.* We designed and

constructed an achromatic interferometer for recording an intensity autocorrelation (the same interferometer will be used in the FROG measurement).



In FY2001, we used this apparatus to record the first autocorrelation of high harmonic radiation up to order 9. The figure shows a typical autocorrelation trace of the 5th harmonic light. These harmonics are correlated to the pulse length of the mid-infrared fundamental field. Our studies show that the temporal compression of these harmonics is consistent with perturbative theory and compression factors as large as 3 have been observed.

The temporal coherence time of the high harmonics were also measured with minor modifications to the interferometer. The results of these measurements are not fully analyzed, but preliminary analysis suggests that the high harmonic light is transformed limited. Furthermore, the intensity profile, coherence and spectroscopy will form a complete picture of the physics that will supply us with the roadmap for attosecond pulse generation. The results obtained in FY2001 are being prepared as a manuscript for Physical Review Letters.

We currently have solved the major technical issues associated with the measurement of high harmonic radiation. Our work towards attosecond pulses will continue under a newly-funded DOE program (FWP4543) entitled "Generation and Characterization of Attosecond Pulses" derived from this LDRD.

SPECIFIC ACCOMPLISHMENTS:

Three papers on the high harmonic physics have been published in referred journals, these include Phys. Rev. Lett. **83**, 5270 (1999), Phys. Rev. Lett. **84,** 2822 (2000) and Laser Physics **11**, 226 (2001).

"High Harmonic Generation at Long Wavelengths," B. Sheehy, J. Martin, L.F. DiMauro, P. Agostini, K. Schafer, M. Gaarde, and K.C. Kulander, Phys. Rev. Lett. 83, 5270 (1999).

"Strong Species Dependence of High Order Photoelectron Production in Alkali Metal Atoms," M.B. Gaarde, K.J. Schafer, K.C. Kulander, B. Sheehy, Dalwoo Kim, and L.F. DiMauro, Phys. Rev. Lett. 84, 2822 (2000).

B. Sheehy, T. Clatterbuck, C. Lynga , J.D. Martin, Dalwoo Kim, L.F. DiMauro, K.J. Schafer, M.B. Gaarde, P. Agostini and K.C. Kulander, "Strong Field Physics in a Scaled Interaction," Laser Physics 11, 226 (2001).

In preparation (tentative title): "Temporal Characterization of High Harmonic Radiation," T. Clatterbuck, C. Lynga, J. Martin, B. Sheehy, L.F. DiMauro, P. Agostini, and K. C. Kulander, for Phys. Rev. Lett.

L.F. DiMauro in FY2002 received new funding (FWP4543) from DOE in response to a DOE initiative on "Novel X-ray Sources." The grant entitled "Generation and Characterization of Attosecond Pulses" is a consortium of both national laboratory and university investigators.

LDRD FUNDING:

FY 1999	$109,251
FY 2000	$ 77,988
FY 2001	$ 71,812

Study of Catalysts for SOx and NOx Decomposition using Synchrotron Radiation

Jose A. Rodriguez *99-62*

PURPOSE:

There are two main goals in this project. The first one deals with the study and design of new catalysts for the removal or destruction of sulfur and nitrogen oxides (DeSOx and DeNOx operations). The second one focuses on the development of synchrotron-based techniques for the characterization of these catalysts in-situ under realistic industrial conditions.

APPROACH:

Nowadays a major effort in environmental catalysis is focussed on reducing the content of sulfur and nitrogen oxides in the atmosphere. SO_2 and NO_2 are major air pollutants produced during the combustion of fuels in automotive engines, factories, and power plants. There is a clear need to develop sorbents/catalysts with a high efficiency for DeSOx and DeNOx operations. Oxides can be quite useful in this respect.

In previous years our research group has developed an expertise in the use of synchrotron-based methods for examining the properties of oxides and the behavior of sulfur on solid surfaces. The combination of several experimental techniques (photo-emission, x-ray absorption near-edge spectroscopy, time-resolved x-ray diffraction) and theoretical methods (density-functional calculations) allowed a detailed study of fundamental problems for the design of a new generation of DeSOx and DeNOx catalysts.

TECHNICAL PROGRESS AND RESULTS:

FY 2001 was the final year in the LDRD. The main focus of the research was on the catalytic performance of several mixed-metal oxides. Particular attention was paid to metal-doped MgO and several molybdates of the $AMoO_4$ type (A= Fe, Co or Ni). Using a combination of experiment and theory, fundamental principles were established for the cleavage of S-O and N-O bonds on oxide surfaces. These basic principles helped in the design of catalysts that are inexpensive, safe for handling, and environmentally friendly.

In addition, our studies proved that x-ray near-edge spectroscopy (XANES) is an excellent technique for studying the chemistry of SO_2 and NO_x species on oxide surfaces. When compared to other techniques it allows an easy and precise identification of reaction intermediates.

SPECIFIC ACCOMPLISHMENTS:

"DeNOx Reactions on MgO(100), $Zn_xMg_{1-x}O(100)$, $Cr_xMg_{1-x}O(100)$, and $Cr_2O_3(0001)$: Correlation between Electronic and Chemical Properties of Mixed-Metal Oxides," J.A. Rodriguez, M. Perez, T. Jirsak, L. Gonzalez, A. Maiti and J.Z. Larese, J. Phys. Chem. B, 105 (2001) 5497-5005.

"Environmental Catalysis and the Chemistry of SO_2 on Oxide Surfaces: Fundamental Principles for the Cleavage of S-O Bonds," J.A. Rodriguez, Ciencia, 9 (2001) 139-154 (invited).

"Coadsorption of Sodium and SO_2 on MgO(100): Alkali Promoted S-O Bond

Cleavage," J.A. Rodriguez, M. Perez, T. Jirsak, L. Gonzalez, and A. Maiti, Surf. Sci. 477 (2001) L279-L288.

"Reaction of SO_2 with Pure and Metal-doped MgO," J.A. Rodriguez, T. Jirsak, L. Gonzalez, J. Evans, M. Perez, and A. Maiti, J. Chem. Phys.115 (2001) in press.

"The Behavior of SO_2 on Oxide Surfaces: Density Functional and Photoemission Studies," Department of Physics, California State University at Northridge, February 2001.

"DeNOx and DeSOx Reactions on Oxide Surfaces: Fundamental Principles for the Design of Catalysts," Catalysis Consortium Meeting/Molecular Simulations Inc, San Diego, California, March 2001.

"Behavior of Mixed-Metal Oxides in DeSOx processes: Density Functional and Synchrotron-Based Studies," Accelrys Seminar on Quantum-Mechanical Modeling in "Behavior of Mixed-Metal Oxides in DeSOx processes: Density Functional and Synchrotron-Based Studies," Accelrys Seminar on Quantum-Mechanical Modeling in Catalysis, Princeton, June 2001.

"Desulfurization Reactions on Oxide Surfaces: Fundamental Principles for the Design of Catalysts," Venezuelan Institute of Scientific Research (IVIC), Altos de Pipe, Venezuela, November 2001.

"Desulfurization Reactions on Oxide Surfaces: Fundamental Principles for the Design of Catalysts," Venezuelan Institute of Petroleum (INTEVEP), Los Teques, Venezuela, November 2001.

LDRD FUNDING:

FY 1999	$121,957
FY 2000	$ 48,789
FY 2001	$ 57,458

Probing Extreme QCD: Articulating the Physics Goals of an Electron-Relativistic Heavy Ion Collider (eRHIC) at BNL

Raju Venugopalan *00-06*
A. Deshpande
G. Garvey
T. Ludlam
L. McLerran

PURPOSE:

An Electron-Relativistic-Heavy-Ion Collider (eRHIC) can probe a novel, highly non-linear regime of high-parton densities in Quantum Chromodynamics (QCD) at very small Bjorken x and Q^2 on the order of several GeV^2. Comparable parton densities at an electron-proton (ep) collider would require Bjorken x's that are three to five orders of magnitude smaller. Moreover, an Electron-Nucleus (eA) collider provides a unique opportunity to study the space-time structure of scattering in QCD. We have shown that the matter probed in these collisions may be a Color Glass Condensate (CGC) and have proposed signatures of this matter. We have shown how an eA collider provides a precise understanding of matter currently studied in Nucleus-Nucleus (AA) collisions and to be studied in Proton-Nucleus (pA) collisions at RHIC. Polarized electron-proton collisions are feasible at eRHIC. Our studies show that eRHIC can extract the gluon contribution to the proton spin, to high precision, from a variety of final states. Several studies have also been initiated which investigate generalized parton distributions and spin fragmentation functions. Semi-inclusive final states of interest in eA and polarized e-polarized p collisions may be of interest in different kinematic regions. This may require exploring several detector and accelerator options for eRHIC.

APPROACH:

The behavior of QCD, the theory of strong interactions, is not well understood at very high energies or equivalently at high-parton densities. A powerful analogy is Quantum Electrodynamics (QED) where the theory was known to be correct for a long time but remarkable and fundamental many body phenomena such as phase transitions, superconductivity, etc. were not understood. Starting with the Hadron Electron Ring Accelerator (HERA) collider at Deutsch Electron Synchrotron (DESY) in Germany, a regime of high-parton densities became available, thereby making the study of similarly remarkable collective phenomena in QCD feasible.

Nuclei provide a natural source of high-parton densities. This is why eRHIC makes eminent sense since it provides a tremendous amplification in parton densities. In heavy ion collisions at RHIC the threshold of high-parton densities is being approached; thus, eRHIC can help solidify what we learn from RHIC.

How the spin of the proton is generated is another deep puzzle in QCD. It has been known for some time that gluons carry a significant fraction of the spin but how much is not known. The gluon contribution (termed Delta G) will be measured at RHIC (in pp collisions) for the first time. eRHIC provides an opportunity to measure Delta G with high precision (at very small x's and through a variety of observables) by colliding polarized electron and proton beams. This possibility has triggered a lot of interest in the polarized physics community, and the eRHIC community has

merged with this community to form the EIC (Electron Ion Collider) collaboration.
The scope of the investigation is a) to clarify the terra incognita of novel states of matter at high-parton densities and to provide a basis for these in current experiments, b) to explore signatures of the space-time structure of QCD matter, and c) to compute the degrees of precision (relative to studies at other colliders) with which the spin structure of the nucleon can be elucidated. The studies reported here are primarily conceptual in kind involving analytical as well as Lattice and other Monte Carlo techniques.

TECHNICAL PROGRESS AND RESULTS:

In FY2000, there were several studies (reported at conferences at BNL, Yale, and MIT) which related saturation phenomena at high-parton densities to observables at HERA and made preliminary predictions for eRHIC. Also, on the spin front some preliminary studies were performed (and also reported at aforementioned workshops).

A remarkable recent progress in FY01 has been the understanding of high-parton densities as a Color Glass Condensate (CGC). This is work done by one of us (Larry McLerran with Edmond Iancu, Andrei Leonidov, and Elena Ferreiro) based on a breakthrough by a former post-doc here, Yuri Kovchegov (currently at the Univ. of Washington). These are the first rigorous studies in the non-linear regime of QCD. Venugopalan (with Alex Krasnitz and Yasushi Nara) has been exploring how the CGC melts in a nuclear collision. Important technical progress includes implementing the SU(3) gauge group and open boundary conditions. If the RHIC data show evidence of a CGC, that provides a formidable argument to further pursue such studies with eRHIC/EIC. The first indications from work by Kharzeev, Nardi, Levin, McLerran, and Venugopalan are that such evidence is present in the first RHIC data. These results, presented at the DNP meeting in Hawaii, have generated tremendous interest in the field.

Important progress has been made in identifying new signatures of the CGC (by Jalilian-Marian, Serbo, Gelis, Dumitru, and Peshier) in a number of final states in eA, pA and AA collisions. Deshpande (with G. Reidel, A. deRoeck) has performed studies of Delta G demonstrating that it can be cleanly measured at eRHIC. A workshop at Trento discussed these results relative to estimates for HERA, Tesla HERA Collider (THERA), and RHIC.

SPECIFIC ACCOMPLISHMENTS:

A. Refereed Publications:

1. A. Krasnitz and R. Venugopalan, Phys. Rev. Lett.86, 1717 (2001).
2. A. Krasnitz, Y. Nara, and R. Venugopalan, Phys. Rev. Lett.87, 192302 (2001).
3. E. Iancu and L.D. McLerran, Phys. Lett. B510, 145 (2001).
4. E. Iancu, A. Leonidov, and L.D. McLerran, Phys. Lett. B510, 133 (2001).
5. E. Gotsman, E. Levin, U. Maor, L.D. McLerran, and K. Tuchin, Nucl. Phys. A683, 383 (2001).
6. E. Iancu, A. Leonidov, and L.D. McLerran, Nucl. Phys. A692, 583 (2001).
7. J. Jalilian-Marian and X.N. Wang, Phys. Rev. D63, 096001 (2001).

B. Conference Proceedings and Lectures:

1. L. McLerran, In Shifman, M. (ed.): At the Frontier of Particle Physics, Vol. 1 637-652.

2. L.D. McLerran, "The Color Glass Condensate and Small x Physics: 4 lectures," arXiv:hep-ph/0104285.

3. R. Venugopalan, "Deeply Inelastic Scattering of Nuclei at RHIC," in Proceedings of 2nd Workshop on Physics with an Electron Polarized Light Ion Collider (EPIC 2000), Cambridge, Massachusetts, 14-16 Sep 2000, Published by American Institute of Physics.

C. Preprints:

1. J. Jalilian-Marian and S. Jeon, arXiv:hep-ph/0110417.

2. A. Dumitru and J. Jalilian-Marian, arXiv:hep-ph/0111357.

3. J. Schaffner-Bielich, D. Kharzeev, L.D. McLerran, and R. Venugopalan, arXiv:nucl-th/0108048.

D. Invited and Plenary Talks:

1. R. Venugopalan, Invited talk at the HERA3 workshop at Durham, England, December 6th-7th, 2001.

2. Invited talk, *International Conference on the Physics of the Quark Gluon Plasma*, Ecole Polytechnique, France, September 3rd-7th, 2001.

3. Invited talk, *Statistical QCD*, Bielefeld, Germany, August 26th-30th, 2001.

4. Invited talk, *Gordon Conference on QCD at High T, High mu and Small x*, Newport, July 22nd-27th, 2001.

5. Invited talk, *ThermalFest*, BNL, July 20th-21st, 2001.

6. Seminar at McGill University, April 26th, 2001.

7. Seminar at Ohio State University, April 16th, 2001.

8. Colloquium at Iowa State University, April 9th, 2001.

9. Invited talk at Workshop on Lepton Scattering, Hadrons, and QCD, March 26th-April 6th, 2001, Adelaide, Australia.

10. Plenary talk, *Quark Matter 2001*, Stony Brook, January 15th-19th, 2001.

11. Plenary talk at DNP meeting, Williamsburg, October 2000.

12. Plenary talk at EPIC workshop, MIT, September 14th-16th, 2000 1) Invited talk, *International Conference on the Physics of the Quark Gluon Plasma*, Ecole Polytechnique, France, September 3rd-7th, 2001.

LDRD FUNDING:

FY 2000	$83,928
FY 2001	$69,851

Rapid Real-time Measurement of Aerosol Chemical Composition

Yin-Nan Lee *00-25A*

PURPOSE:

The main objective of this research project is to develop a fast in-situ real-time analytical technique to quantitatively determine the chemical composition of ambient aerosol particles. The chemical species to be measured include inorganic and organic ions and the total organic carbon. The fast data acquired (time resolution better than 10 min on the ground and 3 min on aircraft) are to provide crucial information needed to understand the sources and chemical evolution of aerosol particles and their properties that impact the environment and human health.

APPROACH:

Ambient aerosols were collected using a newly invented technique, particle-into-liquid-sampler (PILS) which grows submicron to micron size particles into supermicron droplets under supersaturated conditions. The resulting droplets are collected using a single orifice impactor. The liquid sample is washed off from the impactor and transported to the analytical instruments using a constant carrier liquid flow. Currently, 2 ion chromatographs (IC) are used, respectively, to determine cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and anions (NO_3^-, SO_4^{2-}, formate, oxalate). Total organic carbon (TOC) was determined using a newly acquired TOC instrument (Ionics, Inc., model 800 Turbo). Both organic and carbonate carbon are oxidized to CO_2 using UV oxidation aided by ammonium persulfate. The resulting CO_2 was detected conductometrically. A new PILS-IC-TOC instrument was constructed and tested during the NE-OPS (Northeast Ozone and Particle Study) field program in Philadelphia, PA. Dr. Xiaoying Yu, a postdoctoral associate, has been working on this project since April 2001.

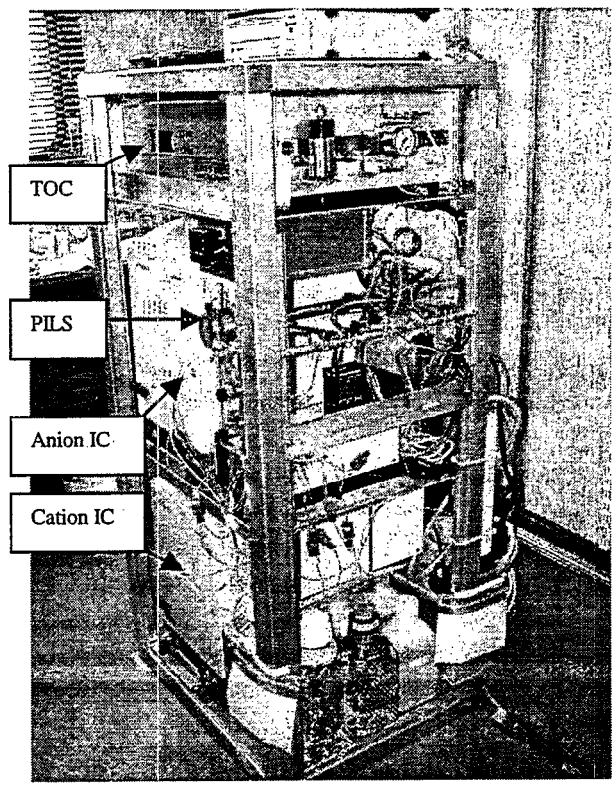


Figure 1. The PILS-IC-TOC system deployed during the 2001 NE-OPS field study in Philadelphia, PA.

TECHNICAL PROGRESS AND RESULTS:

A PILS-IC instrument was developed in FY2000 and was deployed on the DOE G1 aircraft during the Texas Air Quality Study in Houston, August-September, 2000. Three minute data were collected and the total ion mass concentration of the aerosols were compared to the total aerosol mass concentration calculated using the number/size distribution determined by an optical particle counter (PCASP, Particle Measuring System, Boulder CO) and an assumed density. A good agreement was found between these two measurements

during periods when inorganic ions were the dominant aerosol components, lending support to the reliability of the PILS-IC measurement.

During FY2001, we extended the analytical capability of the PILS-based system by incorporating a Total Organic Carbon instrument to determine the total organic content of aerosol particles. A new PILS sampler was constructed which was equipped with an inlet for a PM2.5 size cutter (to sample only particles with an aerodynamic size of 2.5 μm or smaller) and two denuders in series to remove gaseous HNO_3, SO_2, and NH_3. This PILS-IC-TOC system was deployed during the NE-OPS study in Philadelphia, PA, July 13-30, 2001 (Figure 1). The instrument performed well, and the concentrations of TOC and inorganic ions collected during a three-day period between 7/16/01 and 7/19/01 are shown in Figure 2. (The organic fraction shown in the figure represents an upper limit as no organic vapor denuders were used.) The fast data collected are crucial to gaining an improved understanding of aerosols in terms of sources, chemical evolution, physical and chemical effects on the environment and human health.

For FY2002 we anticipate the following added results and milestones. First, we will attempt a mass closure experiment by comparing the aerosol mass concentration determined by the PILS instrument with that measured by a TEOM (Tapered Element Oscillating Microbalance). This study will test the PILS instrument's ability in capturing the major portion of the aerosol mass. Second, we will enhance the analytical capability of the PILS system by implementing chromatographic analysis of the samples to determine the functionalities of the aerosol organic components. This chemical information will help to identify the precursors of secondary organic aerosols and their relationship to photochemistry of volatile organic compounds. Either HPLC (high performance liquid chromatography) or CE (capillary electrophoresis) will be used for this purpose. Plans are also being made to deploy the PILS-IC-TOC instrument on the DOE G1 aircraft along with other aerosol instruments (e.g., size spectrometer, nephelometer, and a particle soot absorption photometer) to perform apportionment of the optical extinction of aerosol particles.

This project does not involve animal vertebrates and/or human subjects.

SPECIFIC ACCOMPLISHMENTS:

A new PILS instrument, which incorporated a total organic carbon measurement technique, was constructed and successfully deployed during a Northeast Ozone and Particle field study. The total organic content of aerosol particles was measured at a high time resolution (~6 min), representing an order of magnitude improvement over the currently available technique. A patent application for the PILS invention has been petitioned by BNL. A paper reporting the PILS instrument has appeared recently: A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. R.J. Weber, D. Orsini, Y. Duan, Y.-N. Lee, P. J. Klotz and F. Brechtel. Aerosol Sci. Technol., 35, 718-727, 2001. An extended abstract reporting the 2000 Houston study has been submitted to the 82nd American Meteorological Society Annual Meeting, Orlando, FL, January 13-17, 2002.

LDRD FUNDING:

FY 2001	$118,156
FY 2002 (budgeted)	$121,000

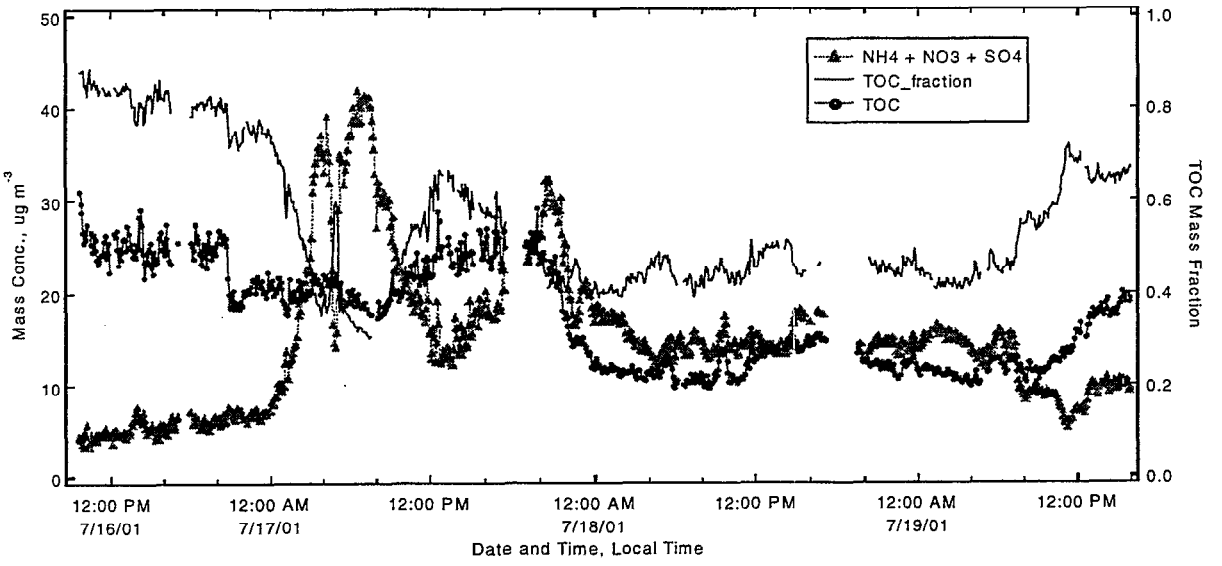


Figure 2. Time series of mass concentration of aerosol total organic carbon (TOC) along with the sum of NH_4^+, NO_3^-, and SO_4^{2-}. The blue trace represents the TOC fraction of the sum of these 4 components.

Novel Techniques to Measure Aerosols and Aerosol Precursors: Multiple Humidity Tandem Differential Mobility Analyzer

Fredrick J. Brechtel *00-25B*

PURPOSE:

The response of ambient aerosols to relative humidity plays a critical role in determining their visibility, health and climate impacts. Current techniques do not have sufficient time response and cannot reveal how chemical composition influences the water uptake properties of aerosols. The objective of this project is to develop a new instrument capable of rapid, size-resolved measurements of aerosol water uptake that can be deployed on-board research aircraft during missions over heavily polluted urban areas. Successful implementation of the new measurement system will provide unique future funding opportunities and position BNL at the forefront of integrated studies of aerosol physical, thermodynamic and chemical properties.

APPROACH:

Over the past several decades traditional Tandem Differential Mobility Analyzer (TDMA) techniques have been used to measure the size-resolved water uptake properties (hygroscopicity) of ambient aerosols. Previous studies in urban areas have demonstrated that at any given size, particles typically contain multiple chemical compounds leading to complex hygroscopic properties. The TDMA requires multiple hours to obtain water uptake information on several different particle size classes at different relative humidities (RH); this time scale is much too long for aircraft observations where changes in aerosol properties are often observed over minute time scales.

To address the need for rapid aircraft measurements of particle hygroscopic growth, a new method is proposed to study multiple particle sizes in parallel at several different RHs. The technique involves two scanning multiple particle mobility spectrometers in parallel to simultaneously select different size particles that are exposed to a coordinated time-varying RH within humidifiers placed between the sets of spectrometers. The first set of spectrometers selects the various dry particle sizes; the exiting particles are then humidified, and the grown droplets are then sized using the second set of spectrometers. A post-doctoral researcher, Gintautas Buzorius, is a key collaborator on the project.

TECHNICAL PROGRESS AND RESULTS:

The prototype instrument design and initial construction began in FY 2000, with testing of a traditional TDMA, humidification techniques and new data acquisition software and hardware. The prototype involved a scanning RH system with only two mobility spectrometers. During FY 2001, the sizing capability of the second spectrometer of the prototype was improved by employing a scanning voltage system, increasing the time resolution of hygroscopic growth measurements by more than one order of magnitude. New data acquisition software was completed, control algorithms for RH and spectrometer control were revamped and optimized, and the system was tested with calibration aerosols having known chemical composition and hygroscopic properties. The prototype was deployed at a surface site during the Aerosol Characterization Experiment-Asia (ACE-

Asia) on Cheju Island, Republic of Korea to make rapid, size-resolved measurements of particle hygroscopic growth in conjunction with single particle chemical composition measurements using a BNL single particle mass spectrometer (BNL-MS). This field deployment represented an important milestone in our understanding of the relationships between the hygroscopic and chemical properties of ambient aerosols. Merging the two instrumental techniques allowed both instruments to sample the same particles simultaneously, a feat that had heretofore never been accomplished. These measurements demonstrated that chemical species typically considered non-hygroscopic undergo chemical reactions in the atmosphere that increase their hygroscopicity.

Whereas current TDMA techniques require approximately 6-8 hours to obtain information on the hygroscopic properties of a representative number of different size classes at different RHs, the current version of our prototype can provide the same information in about one hour. One technical milestone planned in FY 2002 is to employ the parallel mobility spectrometers so that multiple, dry particle populations can be selected simultaneously, thereby reducing the time required to scan particle size and RH to a few minutes.

SPECIFIC ACCOMPLISHMENTS:

The following peer-reviewed publications are related to this activity and represent work accomplished prior to FY 2000:

F. J. Brechtel and S. M. Kreidenweis, Predicting Particle Critical Supersaturation from Hygroscopic Growth Measurements In the Humidified TDMA. Part I: Theory and Sensitivity Studies. Journal of the Atmospheric Science, **57**, 1854-1871, 2000.

F. J. Brechtel and S. M. Kreidenweis, Predicting Particle Critical Supersaturation from Hygroscopic Growth Measurements In the Humidified TDMA. Part II: Laboratory and Ambient Studies. Journal of the Atmospheric Sciences, **57**, 1872-1887, 2000.

The following manuscript has been submitted for publication in the peer-reviewed literature:

G. Buzorius, A. Zelenyuk, F. Brechtel, and D. Imre, Simultaneous Observations of Single Particle Size, Hygroscopicity and Chemical Composition by Coupled HTDMA-Mass Spectrometry. Geophys. Res. Lett., submitted Oct. 2001.

The following conference presentations were made related to the project:

F. J. Brechtel, A. Zelenyuk, D. Imre, and G. Buzorius, First Simultaneous Particle Size, Hygroscopicity and Composition Measurements by Coupled HTDMA-MS. Paper presented at the AAAR conference, Portland, OR, Oct. 2001.

F. J. Brechtel, G. Buzorius, C.-H. Jung, J.-Y. Kim, S.-N. Oh, A. Zelenyuk, D. Imre, P. Chuang, and H. Swan, Aerosol Physical and Chemical Properties at Cheju Island, Korea During ACE-Asia. Poster presented at the ACE-Asia data workshop, Pasadena, CA, Oct. 2001.

LDRD FUNDING:

FY 2001	$117,080
FY 2002 (budgeted)	$121,000

Nanocomposites of Silicon Polymorphs and Related Semiconductor Systems

David O. Welch *00-27*

PURPOSE:

Obtain a detailed understanding of the mechanisms of formation and the properties of nanocrystalline dispersions of metastable high-pressure polymorphic phases of Si and related semiconductor systems in normal diamond-cubic matrices, produced by shock-induced transformations resulting from high-velocity thermal-spray processing. This understanding can be achieved by high-resolution transmission electron microscopy and theoretical analysis, coupled with experimental measurements of opto-electronic properties. The technological promise of this process is that it is a potentially cheap and convenient way of synthesizing coatings for materials which exhibit novel functional behavior. The scientific issues addressed concern factors which influence stress-induced phase transformations and factors which control retention of the metastable nanoscale phases. This requires an understanding of the stress-induced reaction pathways, the kinetics of relaxation reactions, and the role of retained internal stresses.

APPROACH:

This project is a collaboration between the Material and Chemical Sciences Division, Energy Sciences and Technology Department at Brookhaven National Laboratory and the National Science Foundation funded Materials Research Science and Engineering Center (MRSEC) for Thermal Spray Research at the State University of New York at Stony Brook. The group at SUNY-SB demonstrated that thermal spray methods can be used to generate thick films of nanoscale composites of various polymorphic forms of Si. Si exhibits a number of high-pressure polymorphs, and upon depressurization, several metastable polymorphs, some metallic and some semiconducting are observed to result. It can be demonstrated that anisotropic shock synthesis, by means of thermal spray techniques, can be used to synthesize a fine dispersion (2-5 nm) of these metastable phases in a diamond-cubic matrix. The nature of the phases present, their size, and distribution depend on the characteristic velocity of the thermal spray process and on the orientation of the Si crystal substrate. This ability to produce nanoparticles of various metastable high-pressure phases of Si and other similar materials in a diamond-cubic matrix present an opportunity to study the mechanism of phase transformations in semiconductors, as well as to study the properties of nanometer-size dispersions and their potential utility as opto-electronic materials. Furthermore, the application of this method to several semiconductor systems (C, Si, Ge, CdTe, CdSe, and BN) can help elucidate the role of such material factors as ionicity and metallicity.

The capabilities at BNL for transmission electron microscopy (TEM) and theoretical analysis greatly accelerates the progress in understanding the mechanisms of formation and the physical properties of the nanocomposite system. Detailed TEM studies of the crystallographic and nanoscale structure of nanocomposites of group IV elements, as well as related III-V and II-VI compounds, will be performed. Accompanying this is the need for theoretical studies of possible mechanisms and kinetics of the nanocomposite formation mechanisms and of some of the physical properties of the nanocomposites. The primary personnel involved at BNL are

Yimei Zhu (electron microscopy), D.O. Welch (theory), and M. Schofield (Research Associate, electron microscopy); joint BNL/SUNY-SB R. Goswami (Research Associate, electron microscopy and theory); and at SUNY-SB, S. Sampath, (thermal spray processing), R. Gambino (opto-electronic properties), and J. Parise (Geosciences).

TECHNICAL PROGRESS AND RESULTS:

During FY2000 and FY2001, a series of nanocomposite specimens of Si, Ge, C, BN, CdTe, and CdSe were synthesized using shock deformation induced by high-velocity thermal spray processing. By systematically varying the thermal spray parameters, various shock conditions were obtained, and the resulting phases in the nanocomposites were correlated with shock-induced pressures and temperatures. Detailed TEM studies were made of the nanoscale structure, including crystallography of the stress-induced metastable, nanoscale phases present in the resulting nanocomposites. The density and nature of crystal-lattice defects, such as dislocations and stacking faults, were also characterized. Variations of the nanoscale structure with crystallographic orientation of the single-crystal substrates upon which the high-velocity droplets impinged were observed and characterized. Theoretical analyses of the thermodynamics of transformations in the various systems were conducted, and the importance of the shear components of stress in the phase transformation was established. A theoretical analysis was also made of nucleation kinetics and the importance of heterogeneous nucleation of phase transformation on shock-induced dislocations was revealed. The effects of ionicity of III-V and II-VI compounds and the tendency to metallization of the group IV elements on the nature and extent of the metastable phase formation and retention were investigated.

SPECIFIC ACCOMPLISHMENTS:

Publications:

"Shock synthesis of nanocrystalline high-pressure phases in Si, Ge, and CdTe by high-velocity thermal spray," J. Parise, R. Goswami, S. Sampath, R. Gambino, H. Herman, Y. Zhu and D.O. Welch in Microcrystalline and Nanocrystalline Semiconductors – 2000, P.M. Fauchet, et al, editors (Materials Research Society, 2001).

"Shock-induced transformations in hexagonal boron nitride by high-velocity thermal spray," R. Goswami, H. Herman, S. Sampath, J. Parise, Y. Zhu, and D.O. Welch, J. American Ceramic Society (In press).

Presentations:

"Shock synthesis of nanocrystalline high-pressure phases in Si, Ge, and CdTe by high-velocity thermal spray," given at the 2000 Fall Meeting of the Materials Research Society (November 27-30, 2000; Boston, MA); and an invited talk entitled, "Melting of Nano-Embedded Particle: The Role of Interface Structure," will be presented at the 131st Annual Meeting of the Minerals, Metals, and Materials Society (TMS), February 17-21, 2002; Seattle, WA.

In addition, this work led to a proposed project, "Phase stability and structural defects in nanoscale transition metal oxides," in the proposed Brookhaven Center for Functional Nanomaterials.

LDRD FUNDING:

FY 2000	$79,117
FY 2001	$59,505

Microvascular Endothelial Cells as Targets of Ionizing Radiation

Louis A. Peña *00-32*

PURPOSE:

This LDRD supports the establishment of *in vitro* models of brain microvascular endothelial cells (EC) for radiobiology studies. A complex variation of the basic methodology which involves co-culture with a second cell type (astrocytes) permits the establishment of *in vitro* models of Blood Brain Barrier (BBB). Unlike the majority of cell culture model systems consisting of immortal transformed cell lines, EC cultures are actually primary cultures which undergo differentiation and senescence affected by many variables such as the composition of the extracellular matrix. Consequently, a significant amount of pilot work is necessary to adapt and establish a model system of this type for a specific new scientific use. Development of EC models will allow us to initiate a new program of basic and applied research of relevance to Radiobiology and Radiation Oncology, using modern cell- and molecular biology techniques. These model systems are not only important for our own project but will also promote future collaborations with other investigators/ projects at BNL (e.g., neuro-imaging drug development [S.J. Gatley], neuro-imaging and the BBB [W. Rooney], microbeam radiation therapy [F.A. Dilmanian], radiation-induced cell death of CNS glial cells [L.A. Peña]).

APPROACH:

A significant portion of radiation injury arising from the therapeutic use of ionizing radiation is attributable damage to blood vessels. Microvascular endothelial cells are the cells of which capillaries are composed, and are the cells which line the inner lumen of large blood vessels (e.g., arteries and veins). With respect to the central nervous system, there is one added level of complexity. Capillaries in the brain and spinal cord consist of ECs possessing intracellular tight junctions that confer a chemical permeability barrier known as the BBB. The ability to modulate the radiation tolerance of ECs in any organ system and in the special case of the central nervous system would be of significant therapeutic utility. Basic research into mechanisms of cellular responses to radiation is, therefore, of significant utility. Much of what is known in this area was done by Radiation Oncology researchers before the advent of modern molecular biology. To apply modern tools to this general problem, reliable *in vitro* models (cell culture) are required. The specific study of blood vessels and angiogenesis (Vascular Biology) is a specialized field in its own, and we need to draw experience from this area in order to apply it to the specific radiobiological questions.

EC cultures and co-cultures grown under various conditions and configurations have been evaluated for this LDRD project. The parameters of interest are cell growth, cell proliferation, cell death, apoptosis, cell differentiation into tube-like structures that resemble normal capillaries, and de novo expression of biochemical markers typical of a differentiated state (e.g., alkaline phosphatase, gamma-glutamyltransferase). The culture variables are requirements for certain growth factors (e.g., VEGF, bFGF), plastic substrates, microporous membrane substrate, Matrigel® coating, and most importantly co-culture of EC with glial cells of the astrocytic type (e.g., primary astrocytes, glioma cell lines).

EC cultures systems of different configurations were irradiated by x-ray or by gamma-ray in a dose range of 5 to 500 cGy using ionizing radiation sources in the Medical and the Biology Departments. In addition, some EC culture systems were subjected to x-ray microbeams (3-100 μm in width) at the X15B and X17B beamlines at the NSLS.

In this period of LDRD support we were also able to obtain an extramural "Targeted Opportunity" special-use grant funded by the Stony Brook Research Foundation, in collaboration with Hong Lau, MD, PhD, of the Department of Radiation Oncology, School of Medicine, SUNY Stony Brook. This enabled us to extend the LDRD project carried out at BNL to utilize a unique core facility at a neighboring academic institution. Thus, human EC cultures in a proliferating and in a quiescent state were irradiated at BNL, mRNA harvested, and then transported to the SUNY Stony Brook Biotechnology Center DNA Microarray Core Facility. There our samples were hybridized to Affymetrix® DNA Chips, and the up- and down- regulation of ~12,000 genes were quantitated.

TECHNICAL PROGRESS AND RESULTS:

First, development of in vitro EC culture systems is nearing completion. Optimization of the parameters described above is nearly complete. In addition, we have settled on two alternate methods for producing a BBB culture system -- one consisting of co-cultured cells grown on top of each other, and the second consisting of EC grown as a confluent monolayer on one surface of a sterile membrane and C6 glioma cells monolayers on the other surface (the membrane contains 3 μm pores permitting limited cell-cell contact in addition to solutes passing from one side to the other).

Second, a series of radiobiological data have been collected on radiation-induced apoptosis in EC monolayers supporting studies on modifying radiation tolerance of EC. We have investigated the use of bFGF as a cytokine-based method of conferring radiation resistance via biochemical stress-signaling pathways common to eukaryotic cells. Moreover, this effort has allowed us to develop a novel class of synthetic bFGF analogs, which we designate F2A. Two lead compounds, F2A3 and F2A4, are the subjects of two Records of Invention and with additional supporting data collected over the next LDRD funding period, we will apply for patent protection for these specific compounds and the class of compounds from which they are conceptually derived. This work has been done in collaboration with Dr. Paul O. Zamora of BioSET, Inc.

The DNA microarray analysis has resulted in anticipated and unanticipated findings. The wealth of data derived from this screen will permit continuation of hypothesis-driven work. For example, many genes involved responses to oxidative stress were upregulated as expected. However, we unexpectedly found that EC release two secreted death inducing ligands (soluble "death signals") in response to irradiation (e.g., TRAIL). The unexpected release of death factors may contribute to a novel mechanism responsible for the so-called bystander effect. Ongoing studies are being done to address this issue.

This project involves perinatal rats as a source of astrocytes for primary culture and is done under IACUC-approved Protocol #198.

SPECIFIC ACCOMPLISHMENTS:

The first year of the LDRD-funded project resulted in data useful for internal purposes, but the current second year of this project

has begun to produce accomplishments of external significance.

First, as an outgrowth of our use of cytokines to modify radiation tolerance of EC, we have developed a class synthetic cytokine analogs. This has led to the filing of two Record of Inventions with the BNL Office of Technology Transfer. [(1.) Peña L.A., Zamora P.O.: A class of synthetic cytokine analogs for surface coatings of medical devices. (2.) Peña L.A., Zamora P.O., Lin X. Synthetic cytokine analogs of FGF-2 for surface coatings of medical devices.]

Second, we have found a corporate/industry partner to develop these novel synthetic analogs. Dr. Paul Zamora, of BioSET Inc. and Dr. Peña are currently preparing a SBIR grant proposal to NIH. This partnership is expected to lead to continuation of the LDRD-funded research on EC but also into other areas of significance to medical devices and wound healing applications.

Finally, portions of this LDRD-supported work have contributed to work leading to two scientific manuscripts for peer-reviewed journals. One has been submitted, and one is in preparation at the time of this writing. [(1.) Peña L.A., Lau Y.H., Makar M.: Lack of Potentiation of Boron Neutron Capture (BNCT) Irradiation by Gadolinium Neutron Capture (GdNCT) in Glioma and Endothelial Cells *in vitro*. *Submitted.*, 2002; (2.) Lin X., Lau Y.H., Peña L.A.: DNA Microarray Analysis of Radiation Effects on Endothelium. *In Preparation.*, 2002]

LDRD FUNDING:

FY 2000	$ 82,633
FY 2001	$100,622
FY 2002 (budgeted)	$ 60,000

The Structure of Membrane Proteins: Monolayers and Thin Films

Ben Ocko *00-40*
D. Schneider

PURPOSE:

To investigate the structure, oligomeric state, and interactions of membrane integral proteins by surface x-ray scattering techniques with the twin goals of developing new methods for obtaining structural information and to obtain fundamental information on the nature of protein membrane interactions. By varying the protein to membrane component concentration, detailed information can be obtained on the structure and on the protein-membrane interactions. An important aspects of our studies is to map out the phase behavior of membrane proteins as function of multiple environmental parameters including temperature, vapor pressure, surface pressure, solution phase conditions (salt, pH, etc.), and lipid terminal group interactions. These environmental conditions will provide for control of the internal protein conformations lead to correlations of these internal conformations with biological activity.

APPROACH:

The Physics Department X-ray Scattering Group has a significant effort devoted to understanding the structure of liquid/vapor interfaces and maintains a Liquid Spectrometer at the NSLS and APS to carry out these studies. Langmuir monolayers (monolayer film on a liquid subphase) provide an ideal environment for studying biological membranes. The molecular area and surface pressure can be accurately controlled which provides a degree of freedom not available in the bulk. In addition, the surface provides preferential alignment. Our approach is to use x-ray reflectivity and grazing angle diffraction to study the adsorption of integral membrane proteins.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, we received the specialized x-ray Langmuir trough that was ordered in the previous year. This allowed us to resume investigations which were on hold since August 2000 when our previous x-ray trough (on loan) was returned.

Investigations on Alpha-helical bundles and Vpu (defined below), in collaboration with Kent Blasie's group at the University of Pennsylvania, were resumed. In addition, studies of Langmuir monolayers of saturated and unsaturated fatty acids, both single component and mixtures were completed, and a draft of a paper is being circulated among the coauthors. Studies of the adsorption of poly-L-lysine, first carried out on a phsopholipid monolayer were extended to fatty acids. Studies on Sphigomyelin with David Vaknin (Iowa) were completed, leading to a publication in the Journal of Biophysics. Studies of protein adsorption on metal chelating liquids were initiated with Michael Kent (Sandia Laboratory), and a paper was submitted to Langmuir. Finally, the first studies of the structure of a Langmuir monolayer on a mercury surface were carried out with Moshe Deutsch (Bar Ilan). A more detailed summary of specific projects follows.

Alpha-helical bundles can provide a structural framework for binding specific prosthetic groups at selected locations to

mimic a number of functions exhibited by biological proteins, including vectorial electron transfer. In order to realize device application it is necessary to vectorially orient an ensemble of such peptides. Thus, the di-helices were rendered amphiphilic via the covalent attachment of a C16 hydrocarbon chain to their amino terminus. The association between di-helices is directed via designed attractive electrostatic interactions between the polar faces of the amphipathic helices. This association to form the four-helix bundle is pH-dependent as expected and does not occur in the absence of the directed attractive electrostatic interactions.

The human HIV-1 genome encodes six accessory proteins. Vpu, one of those accessory proteins, is an 81 amino acid phosphoprotein with an N-terminal hydrophobic domain and a C-terminal hydrophilic domain. The biological function of Vpu concerns two different activities, the enhancement of the release of virus from the infected cell surface and the triggering of the degradation of the CD4 molecule in the endoplasmic reticulum. The enhancement of virus release is dependent on the transmembrane domain of Vpu which also exhibits nonspecific cation channel activity. In the case of degradation of CD4, the specific virus receptor on the cell surface, the hydrophilic domain of Vpu interacts with the cytoplasmic domain of CD4 thereby triggering the proteolysis of CD4. We have carried out an x-ray reflectivity study of Langmuir monolayers of a pure phospholipid, its mixtures with Vpu at the water/air interface. The reflectivity data as a function of decreasing lipid/protein mole ratio clearly indicates the mixing of the two components in the plane of the Langmuir monolayer in spite of the saturation of the long lipid hydrocarbon chains, consistent with the disordering of gel-phase domains as demonstrated directly by GID. Comparison of the electron density profiles as a function of increasing Vpu/phospholipid mole ratio at a constant, relatively high surface pressure of 45mN/m clearly indicated the contribution of the protein to the monolayer profile structure. Our interpretation of these profiles suggested that the transmembrane helix was localized within the hydrocarbon chains of the host phospholipid monolayer oriented normal to the plane of the monolayer while the amphipathic helices of Vpu's cytoplasmic domain lie in the subphase parallel to the monolayer plane on the surface of the polar headgroups at this surface pressure.

GID studies were completed on a stearic acid monolayer and for two mixtures of stearic and elaidic acid. The pure stearic acid exhibits an L2 phase below pressures of 16 mN/m. The 70% stearic acid mixture appears to exhibit a phase separation between a region rich in stearic acid and one rich in elaidic acid. Although the phase of the stearic rich region is identical to pure stearic acid at low surface pressures, above 10mN/m the stearic rich region exhibits an L2' phase, where the direction of tilt has shifted by 30 degrees with respect to the L2 phase. GID patterns at the same surface structure, albeit at different molecular areas. Subsequent Brewster Angle Microscopy studies provide support to our findings of phase separation.

In addition, we carried out studies of the adsorption of poly-L-lysine, a protypical cationic protein, at the surface of a phosphatidylserine monolayer deposited on a phosphate buffer subphase (in collaboration with Stuart McLaughlin at Stony Brook). The very cationic protein should strongly bind to the acidic lipid; however, we did not observe any significant change in the surface normal density profile

after the addition of the protein. Similar results were also obtained with stearic acid.

This project is progressing through collaborations, and several one-two month visitors will be brought to BNL during the next year.

SPECIFIC ACCOMPLISHMENTS:

Sphingomyelin at the air-water interface, D. Vaknin, M. Kelley, B.M. Ocko, Journal of Chemical Physics. **115**, 7697 (2001)

Orientational Distributions of the Di-a-helical Synthetic Peptide ZnPPIX-BBC16 in Langmuir Monolayers by X-ray Reflectivity and Polarized Epifluorescence. A. Tronin, J. Strzalka, X. Chen, P.L. Dutton, B.M. Ocko, K. Blasie, Langmuir **17**, 3061 (2001)

Structural Studies of the HIV-1 Accessory Protein Vpu in Langmuir Monolayers: Synchrotron X-ray Reflectivity, S. Zheng, J. Strzalka, C. Ma, S. Opella, B.M. Ocko, J.K. Blasie, *Biophysical Journal.* **80**, 1837 (2001)

Segment concentration profile of myoglobin adsorbed to metal ion-chelating lipid monolayers at the air-water interface by neutron reflection, Langmuir (submitted)

LDRD FUNDING:

FY 2000	$16,566
FY 2001	$ 636
FY 2002 (budgeted)	$50,400

Understanding the Pathways of Ubiquitin Dependent Proteolysis

Maria Bewley *00-43*

PURPOSE:

Using two model systems, this LDRD probes the role of protein:protein interactions in cellular function. The mechanisms of DNA repair and electron transfer are being investigated. Understanding the rules that guide low and high affinity protein:protein interactions will have wide ranging implication for understanding the functions of the cell, as well as aid in designing of biological systems that have specific properties.

APPROACH:

Understanding the function of multi-component systems is often incomplete because typically individual proteins have been studied in isolation rather than in the context of a biologically relevant complex. There will be a focus on two systems; the pathway of mammalian DNA double strand break repair the electron transfer pathway of flavin adenine dinucleotide (FAD) requiring enzymes.

Double strand break (DSB) repair is crucial to the survival of a cell, yet its mechanism is relatively poorly understood. Since addressing this question is a huge undertaking, a large number of approaches must be tried. This LDRD is using a "divide and conquer" strategy to obtain structural information about the proteins involved. Protein:protein interactions play a crucial part in the regulation and action of repair, and some of the players are already known including DNA protein kinase (DNA-PK), Ku70:80, XRCC4 and DNA ligase IV.

FAD-requiring electron transfer pathways are ubiquitous in nature. For example, nitrate assimilation in plants uses the assimilatory nitrate reductase pathway, which involves the FAD-containing enzyme nitrate reductase (NR). Fatty acid desaturation, which occurs in all mammals, involves electron transfer from the FAD-containing enzyme, cytochrome b_5 reductase (b5r) to cytochrome b_5. These proteins belong to the ferredoxin:NADP+reductase (FNR) superfamily that includes nicotinamide adenine dinucleotide hydride (NADH) and nicotinamide adenine dinucleotide phosphate hydride (NADPH) requiring enzymes. The electron transfer mechanism is a key unanswered question for this superfamily. Communication between the domains and protein:protein interactions play a key role. In collaboration with Dr. M. Barber at the University of South Florida, protein crystallography to understand this process is being done.

TECHNICAL PROGRESS AND RESULTS:

DSB-repair: Based on earlier work in FY 2000, DNA-PK has been divided up into putative domains. In addition, domains of proteins that are known to interact with DNA-PK have also been identified. Expression of such domains is usually initially tested in prokaryotic expression systems, since they are relatively inexpensive, robust, and fast. However, in FY 2001, despite expansive testing using a variety of tags and constructs, there has been an inability to express sufficient soluble protein for crystallization.

For FY 2002, in collaboration with P. Freimuth, there will be a pursuit for other expression systems such as the eukaryotic

Drosophila expression system and, if soluble protein is obtained, show that a biologically relevant complex has been formed.

Electron transfer: For FY 2000, microcrystals of b5r and NR had been produced. In FY 2001, their structures were solved to 2.0Å and 2.4Å resolution, respectively, and in a complex with their substrate or a substrate analogue. These results showed that the mechanism for electron transfer is different for NADPH and NADH requiring enzymes. Interestingly, a non-productive mode of substrate binding was seen. Based on these results, site directed mutagenesis followed by enzyme characterization and crystallography was used to probe the FAD and NADH binding. By comparing the structures of NADH and NADPH requiring enzymes, variants have been engineered that alter the substrate specificity of b5r to be either bispecific or NADPH requiring.

The reaction of electron transfer occurs very quickly. Therefore, in order to visualize this crystallographically, variants that slow the reaction down but do not affect the affinity of the enzyme for substrate are required. Identification of a number of variants with this property has been made. The ultimate goal of this research is to understand how the complex between b5r and cytochrome b_5 domains is formed. This interaction is weak, but the binding interface has been identified.

The structure of the FAD-binding domain of NR showed that the FAD binds in a novel conformation, seen only in the DNA repair enzyme DNA photolyase. This conforma-tion in NR is likely to be a crystallization artifact, and it can be returned to a 'normal' conformation by the addition of substrate. However, for DNA photolyase it has been argued that the novel conformation is functionally important.

These results will be built upon in FY 2002. Specifically, the acquisition of a stable b5r-cytochrome b_5 complex and a structure for the productive mode of NADH binding will be pursued. A short amount of time will be spent trying to ascertain whether the conformation of FAD in DNA photolyase is biologically relevant. Microspectro-photometry techniques will be employed. If this conformation is an artifact of crystallization, the result will have wide-ranging implications for the DNA-repair field and be controversial.

SPECIFIC ACCOMPLISHMENTS:

DSB-repair: In FY 2001, the available prokaryotic systems were eliminated for expressing domains of DNA-PK.

Electron transfer: The structure of cytochrome b_5 reductase was published in Biochemistry (Bewley et al, 2001. Biochemistry **40**, 13574-13582). The structure of the FAD-binding domain of NR has been submitted to the Journal of Molecular Biology. Variants have been characterized crystallographically and kinetically that probe the cofactor and substrate binding sites, including R91, Y93, and D239. Mutating R91 alters the electrostatic environment of the FAD-binding pocket and changing the conformation of the FAD itself. Converting D239 to a threonine residue changes the specificity of the enzyme to NADPH requiring. Manuscripts for publication in peer-reviewed journals are in preparation for all these structures.

LDRD FUNDING:

FY 2000	$244,247
FY 2001	$216,260
FY 2002 (budgeted)	$215,000

Structural Characterization of DNA-PK, a Human DNA Double-Strand Break Repair Protein

John M. Flanagan *00-44*
C. W. Anderson

PURPOSE:

The goal of this project is to determine high-resolution structures of the DNA repair components involved in Double-Strand Break Repair (DSBs). DSBs are produced by ionizing radiation, and their efficient and faithful repair is essential since the presence of a single unrepaired DSB can result in cell death, or in mammals, cancer. At present, little is known about the detailed mechanism of DSB repair, although this process has important mechanistic implications for modeling the effects of low doses of radiation on cells and in treating human cancers. To date, mechanistic studies of the pathways for DSB repair have suffered from a lack of high-resolution structures for their components. In this project, we will focus on obtaining functional complexes containing DNA-PK_{cs}, a component of the non-homologous end joining pathway for DSB repair that are suitable for crystallographic structure. DNA-PK_{cs} forms a functional hetero-oligomeric complex with two other proteins Ku70K80.

APPROACH:

Non-homologous End Joining (NHEJ) is the major route by which DSBs are repaired in mammals. A number of laboratories, including that of C. Anderson, have begun to identify specific components in this pathway including DNA-PK_{cs}, Ku70Ku80. However, due to the complexities of the system and the fact that most of the components are not available in sufficiently large quantities, our understanding of how DSBs are repaired by this process is still incomplete. With our collaborator, D. Ramsden at the University of North Carolina, we have made strides in obtaining sufficient quantities of DNA-PK_{cs}, Ku70, and Ku80, three of the key components of NHEJ for mechanistic and structural studies. These proteins form a complex that binds to the free DSB ends and is thought to be one of the first steps in identifying broken DNA ends and then recruiting the other components of the repair complexes to these sites. The availability of these reagents has allowed us to prepare defined and stable complexes that are suitable for crystallization trials. Our initial trials will focus on a ~ 700 kDa complex containing DNA-PK_{cs}-Ku70Ku80-DNA. This is a relatively large complex for X-ray crystallography; however, the recent successful determinations of the atomic resolution structures of the ribosome and the *Escherichia coli* RNA-polymerase suggest that it is well within the current capabilities of the beam lines at the NSLS.

TECHNICAL PROGRESS AND RESULTS:

During FY 2001, we have successfully purified the Ku70Ku80 components from the insect Baculovirus expression systems. These studies clearly demonstrate the feasibility of obtaining 5-10 mg of homogeneous Ku70Ku80 for crystallization trials. Our initial biochemical studies with the Ku70Ku80 complex indicate that complex stability is greatly enhanced by the presence of DNA-PK_{cs}, and thus it seems likely to us that co-crystallization efforts will be more likely to yield diffraction quality crystals. Currently, there is no expression system for intact DNA-PK_{cs}, however, previous studies in C. Anderson's

and others laboratories indicate that DNA-PK_{cs} is a relatively abundant protein in mammalian tissues. However, our experience is that during purification of the protein from these sources, the majority of DNA-PK_{cs} is lost and that a significant fraction of the remainder is proteolytically nicked by an endogenous protease. During the second half of FY 2001, we began pilot studies aimed at obtaining larger quantities of extremely pure DNA-PK_{cs} from human placenta, or HeLa cells in tissue culture. Through these efforts we have identified a rapid high-yield procedure to obtain intact DNA-PK_{cs}. Based upon these results it is likely that ~ 5 mg of the enzyme can be obtained from 100L of HeLa cells. In addition to the proposed crystallographic studies, the availability of these quantities of DNA-PK_{cs} and Ku70Ku80 has allowed us to begin, in parallel, mechanistic studies. Using purified components we have begun a thermodynamic analysis of complex formation between DNA ends and Ku70K80 alone and in their ternary complex with DNA-PK_{cs}.

The studies described above form the basis for our crystallization experiments of the DNA-PK_{cs}-Ku70Ku80-DNA complex. In addition, they have opened several new lines of inquiry that are being followed: 1) Kinetic analysis of complex formation; 2) examination of the role of DNA-PK in recruiting other components of the NHEJ repair apparatus. Our current hypothesis is that the DNA-dependent protein kinase activity of DNA-PK_{cs} will play a role in regulating complex formation and perhaps the activities of specific repair components.

SPECIFIC ACCOMPLISHMENTS:

We have identified purification conditions for DNA-PK_{cs} and Ku that will allow us to begin crystallization experiments. We have initiated crystallization experiments that will hopefully lead to a structure of DNA-PK alone or in its ternary DNA-PK/Ku/DNA complex.

LDRD FUNDING:

FY 2000	$44,132
FY 2001	$73,550

New Protein Expression Tools for Proteomics

Paul I. Freimuth *00-45*

PURPOSE:

Our technical objective is to optimize the folding of recombinant proteins into their native, biologically active conformations in *Escherichia coli*, a bacterium which can synthesize proteins in large quantities sufficient for biophysical analyses such as X-ray crystallography. The folding of most proteins *in vivo* is assisted by chaperones, *trans*-acting factors which associate with nascent polypeptides to prevent them from aggregating during the folding process. Methods have been developed to divert most of the cell's protein synthesis machinery (ribosomes) to the production of a single protein species. Under these conditions, synthesis of the normal complement of cell proteins, including chaperones, is reduced. Deficits in chaperone activity may cause mis-folding of many proteins that are over-expressed using high yielding methods (e.g. the bacteriophage T7-based system). Directly modifying proteins enables the production of large quantities that are refractory to over-expression using existing methods.

APPROACH:

Background: In studies leading to this LDRD project, we observed that a human membrane protein (CAR) which usually misfolds in *E. coli* could fold properly if the protein carboxy-terminal end was fused to a particular short peptide derived from the carboxyl-terminal end of the bacteriophage T7 gene 10B protein. This effect is specific, since folding of the protein was not rescued by fusion to other peptides of similar length but different sequence. We formulated the hypothesis that this C-terminal peptide mediates folding either by compensating for the deficit in chaperone activity that results from conditions of protein over-expression (e.g. that the peptide acts synergistically with residual chaperones to assist protein folding), or alternatively, that the peptide mediates folding by a novel, chaperone-independent pathway.

Scope: The scope of our project is (1) to characterize features of this C-terminal peptide that are necessary for its protein folding activity within bacterial cells, (2) to determine the generality of this folding activity and the rules governing what types of proteins can or cannot be folded by this peptide, and (3) to determine whether this peptide can promote renaturation of misfolded proteins *in vitro*.

Methods: To characterize features of the peptide necessary for its protein folding activity, we first analyzed the peptide sequence using computer programs to predict its secondary structure and its similarity to other known peptide sequences. Then, mutations were designed to disrupt specific features suggested by the computer analyses. To assess the universality of this peptide-mediated folding approach, we fused the peptide to a set of yeast proteins selected in the BNL Proteomics Initiative as targets for X-ray crystallographic analysis. In the absence of the peptide, all of these proteins misfold and precipitate during synthesis in *E. coli*. Proteins with or without C-terminal peptide extensions were denatured and then subjected to *in vitro* refolding conditions in parallel to assess whether the peptide extension can increase the yield of soluble, properly folded protein.

TECHNICAL PROGRESS AND RESULTS:

Peptide features: Sequence analysis of the bacteriophage T7 gene 10B terminal 57 residue peptide revealed features which might be essential for the protein folding activity of this peptide. The requirement for these features was tested by site-specific mutagenesis of the peptide and measurement of the effects of the mutations on the protein (CAR D1) folding activity of the peptide. From this analysis we were able to conclude that the protein folding activity of this peptide does not depend on 2 predicted amphipathic α-helices or on sequence motifs which are similar to those in the *E. coli* ssrA-encoded peptide that are recognized by proteins with chaperone activity (e.g. the ssrA peptide is fused to protein fragments that arise during nutrient starvation, and is recognized by the ClpX chaperone and another trans-acting factor, SspB, which together mediate degradation of the protein fragment). The yield of soluble, properly folded CAR D1 also was not decreased when the CAR D1-peptide fusion protein was expressed in an *E. coli* strain lacking the ClpB chaperone; therefore, the peptide does not function in synergy with ClpB.

A trend emerged from this mutant analysis: the CAR D1 folding activity of the peptide extensions appeared to vary with the peptide net charge. Peptide extensions with net charge of -2 had partial activity, whereas peptides with net charge of -5 (or greater) had full activity. The basis for this effect is not fully understood. However, we are testing two alternative hypotheses, one in which the repulsive force between charged peptide domains inhibits protein aggregation thus allowing the nascent proteins to continue along the folding pathway, and another in which the charged peptides alter the protein folding pathway itself, to generate a novel set of folding intermediates that fortuitously have less tendency to aggregate.

Universality of approach: An expanded set of 15 yeast proteins characterized by the BNL proteomics project as being completely or partially insoluble when over-expressed in *E. coli* was tested for enhanced expression by application of our method. Approximately 50% of these proteins responded favorably when fused to the standard peptide extension (e.g. the yield of soluble protein was substantially increased relative to the yield of the corresponding unmodified protein).

In vitro refolding: Refolding reactions were conducted on a test protein with or without the standard carboxyl-terminal peptide extension. Proteins were denatured in 8M urea and then diluted into refolding buffer. Approximately 50% of the unmodified protein precipitated upon dilution of the denaturing agent, whereas the fusion protein remained in solution throughout the procedure and was shown to adopt a protease-resistant stable conformation.

SPECIFIC ACCOMPLISHMENTS:

A manuscript entitled, "Enhanced Folding of Immunoglobulin Variable-Type Domains in *E. coli* by *cis*-acting Peptide Extensions," is in preparation.

Also, a patent application, "Facilitating Protein Folding and Solubility by Use of Peptide Extensions," is also being prepared.

LDRD FUNDING:

FY 2000	$ 41,698
FY 2001	$109,754
FY 2002 (budgeted)	$111,000

High-Throughput Structure Determination for the Human Proteome Project

F. William Studier *00-47*

PURPOSE:

Structural genomics is the systematic determination of 3-dimensional structures of proteins to survey the range of protein structures and functions found in nature. The information and tools generated by structural genomics will provide a framework for understanding biochemical functions and interactions of the proteome of any organism whose genome sequence is known. This capability will further DOE aims such as understanding effects of ionizing radiation and pollutants on human health and harnessing biological processes for bioremediation or carbon fixation. This project addresses a need for informatics database, and computational support for structural genomics in three areas: 1) access to and manipulation of information about proteins found in public databases and web sites; 2) a database and web interface for managing experimental data and work flow for a consortium for high-throughput protein structure determination; and 3) software to reduce the human effort involved in processing x-ray diffraction data from protein crystals to produce high-resolution protein structures.

APPROACH:

We are part of a consortium of scientists at five different institutions piloting high-throughput determination of protein structures, which requires the integration of a wide range of activities, including selecting protein targets; cloning, expressing, purifying and crystallizing the selected proteins; collecting diffraction data at synchrotron sources; processing the diffraction data to determine protein structures; and annotating and depositing structures in the Protein Data Bank. The need for informatics, database, and computational support was apparent from the beginning.

Informatics and database development at BNL is directed by Dawei Lin, assisted by a postdoctoral associate and summer students. The approach is to design systems that gather and organize information from a wide range of public sources, facilitate the capture of locally generated experimental data, and provide status reports needed to manage the workflow. Web interfaces are used to enter data and display reports. Iterative interaction with experimentalists who are selecting protein targets and generating materials and data is crucial to the development of a system that effectively serves the needs of the consortium.

As the production of protein crystals accelerates, the need to streamline the process of obtaining an accurate structural model from x-ray diffraction data becomes increasingly important. Integration and improvement of multiple programs used by crystallographers in the process of model building could potentially reduce direct human involvement in determination of a protein structure from weeks or months to hours or days. Such advances will be essential for achieving the needed efficiency of high-throughput structure determination. Jiansheng Jiang is developing an integrated pipeline of computer programs most commonly used in the structure determination process and is exploring computational approaches to reducing the demand for judgments by a skilled crystallographer in building the amino-acid chain into the electron density map. He interacts with S. Swaminathan, the crystallographer who is directing structure

determination for the structural genomics work at BNL, and with crystallographers who come to use the protein crystallography stations at the NSLS.

TECHNICAL PROGRESS AND RESULTS:

The Structural Proteome Database (SPD) described in last year's report was further developed for use in selection of protein targets for structure determination by the consortium. A set of filters was developed to aid automated selection, and work was initiated on an algorithm for clustering potential targets for relatedness at the domain level.

The Internal Consortium Experiment Database (ICEdb) described in last year's report was further developed through interactions with biochemists and structural biologists. The schema went through further iteration, and cloning and expression information was loaded into the database.

Work on SPD and ICEdb at BNL ended at the end of this LDRD project, with the departure of Dawei Lin for a position with another structural genomics consortium.

The Automated Structure Determination Platform (ASDP) described in last year's report was further developed. It performed successfully in determination of a protein structure at BNL. Further work will be supported by the NIH through the New York Structural Genomics Research Consortium. This pipeline of programs is expected to be used routinely for structure determination by members of the consortium.

SPECIFIC ACCOMPLISHMENTS:

Information provided by SPD and ICEdb facilitated successful applications to DOE for "Analysis of Human Proteins Induced in Response to Ionizing Radiation" and, as part of the New York Structural Genomics Research Consortium (NYSGRC), to become a pilot center in the Protein Structure Initiative of the National Institutes of General Medical Sciences. Further work on ASDP will be supported by the NYSGRC. Work supported by the LDRD was included in an invited presentation (entitled "Protein Production for Structural Genomics") at the International Conference on Structural Genomics 2000, November 2-5, 2000, Yokohama, Japan, and will be included in an invited symposium presentation (entitled "Cloning and Expression of Proteins for Structural Genomics") at the annual meeting of the Brazilian Biochemical Society May 18-22, 2002, Caxambu, Brazil.

LDRD FUNDING:

FY 2000	$ 575,570
FY 2001	$ 284,443

Design Study of a Solid Target for Spallation Neutron Sources

Jerry Hastings *00-49*

PURPOSE:

Neutron scattering research has played a unique role in materials, chemical, and biological science as well as medical research and engineering for the past fifty years. A majority of this research has been carried out at continuous reactor sources that were commissioned in the 1950s and 1960s. However, these sources are rapidly approaching the end of their service and are generally not being replaced. This action has led to a steady decline in the number of days available for performing neutron scattering activities worldwide. Subsequently, there has been an increasing interest in the use of accelerator-based "pulsed" spallation sources. In fact, there are five major new facilities in either the construction phase (at Oak Ridge) or conceptual phase (in Austria and Japan).

These new proposals are aimed at enhancing the performance of the existing spallation sources with proposed increases in source flux of 20X – 50X, and with significant improvements in instrumentation. In order to maximize the effectiveness of these new sources, it is highly desirable to develop a dedicated R&D facility capable of investigating all aspects of spallation neutron production and recovery at power levels in line with these planned sources. The testing would include advanced concepts in target design, reflector/ moderator assemblies, neutron beam transport/shielding and chopper/detector systems. Incorporating such a "test-bed" for new components as well as 'complete' systems at an operating source would be technically difficult if not impossible. Appropriately modified, the AGS accelerator complex at BNL is an ideal place to locate such a facility, since the present performance characteristics can provide as much as 230 kJ per pulse and an average power of as much as 120 kW with only a small incremental increase in funding level.

APPROACH:

The overall strategy to carry out this work will combine physics, fluid dynamics, heat transfer, and stress analysis in an iterative manner. The first step consists of a conceptual design including component sizes and nuclide choices for the various components. This step is followed by a physics analysis that results in the neutron yield and the power deposited in the target. These data are used as input to the thermal, fluid, and stress analyses. If at any of the above steps an unacceptable condition is determined, the process is stopped and repeated with the appropriate corrective action being taken.

We will develop a target to operate at the AGS as a pulsed neutron source to carry out studies on novel reflector, moderator, neutron beam transport, and instrumentation concepts. The brightest possible neutron source consistent with the AGS operating conditions needs to be designed for this purpose. The brightness of a neutron source can be increased by making the source small, thus allowing the moderators and reflectors to be placed as close as possible to it. In the case of a relatively lower power source, such as the one proposed for the AGS, an edge-cooled configuration can be considered. This configuration has the advantage that it can be made of solid target material (no internal cooling), which is ideal for the high-proton energy (24 GeV) at the

AGS. However, due to the potential for an extremely large amount of energy per pulse (~ 230 kJ), it is necessary to design the target with potentially disruptive stress levels in mind. Thus, it is necessary to investigate possible target designs which are consistent with the above two contradictory requirements.

TECHNICAL PROGRESS AND RESULTS:

Two target configurations were investigated; the first a solid iridium rod, and the second consisting of a bed of randomly packed iridium spheres embedded in lead. The first target configuration showed unrealistically high stresses, which would have led to target failure. However, due to the high material density it would have yielded the maximum possible neutron flux. A compromise target configuration consisting of a particle bed embedded in a high boiling point liquid, which could also act as a target, was chosen. The potential advantages of this configuration are:

1) Thermal gradients across solid components (particles) are relatively small compared to the cylindrical target of the desired diameter,
2) The sphere size can be chosen to minimize the effects of thermo-mechanical stress enhancement within the sphere, and
3) The particle bed can potentially disrupt the pressure wave phenomena associated with the short-pulse length.

The disadvantage associated with this target arrangement is that the target density is reduced from its theoretical maximum, and thus the neutron production will be reduced.

An analysis of a particle bed based target was carried out, and the following quantities were estimated:

1) Neutron flux,
2) Pulse shape,
3) Temperature distribution, and
4) Stresses in the central particle and cylindrical containment shell.

The following conclusions could be reached from these results:

1) An edge-cooled target using protons from the AGS is potentially a bright neutron source. This source could be used for a variety of science and engineering based studies,
2) A target design based on randomly packed iridium spheres embedded in lead can overcome the steady state thermal stress concerns of an edge cooled target,
3) The presence of particles in the target can disrupt the pressure waves generated in the target, thus ameliorating the cyclic loads on the containment vessel. Furthermore, the particle size can be varied to minimize the thermo-mechanical stress enhancement within a particle,
4) Residual radioactivity is confined to the target volume; only the cooling water leaves the target assembly. The potential accidental release of radioactivity is thus limited to spills of activated water, and
5) Due to the relatively small size of the target, its eventual disposal is potentially simple compared to large-target designs.

SPECIFIC ACCOMPLISHMENTS:

A paper was presented at the Embedded Topical Meeting on Accelerator Applications at the Reno ANS Meeting on this target design:

H. Ludewig, N. Simos, J. Hasting, P. Montanez, and M. Todosow, "Concept for an Edge Cooled Target at the BNL-AGS," Proc. of American Nuclear Society, Reno, NV. (2001)

LDRD FUNDING:

FY 2000	$301,241
FY 2001	$ 90,921

Development of Superconducting Accelerator Magnets Capable of High dB/dt

Arup K. Ghosh *01-07*

PURPOSE:

The goal of this project is to design, fabricate and test a proof-of-principle *superconducting* dipole magnet, which can be cyclically ramped to 4T in a few seconds with reasonable losses per cycle. When developed, this technology will enable the construction of future rapid-cycling synchrotrons using superconducting magnets such as the one being proposed by the GSI laboratory in Darmstadt, Germany.

APPROACH:

Using the design of the RHIC dipole magnet as a starting point, we have examined the various components of the magnet that contribute to the losses when operating at a dB/dt of ~ 2T/s. These losses occur in several places: inside the superconducting wire, between the wires of the cable, the iron yoke and the bore tube. The losses are due to both hysteresis and eddy-currents. Initial work was done to quantify these losses for a RHIC type dipole and subsequently research focussed on developing a low-loss superconducting wire and cable for a prototype magnet. Table 1 summarizes the calculations for a standard RHIC type dipole.

It is worth noting that this LDRD project is in collaboration with GSI. Collaborators in this study include the following: P. Wanderer, M. Anerella, R. Thomas and A. Jain (BNL), G. Moritz (GSI), M. Wilson and W. Hassenzahl (GSI- consultants).

TECHNICAL PROGRESS AND RESULTS:

Conductor R&D: During FY 2001 considerable progress has been made in the development of a suitable cable similar in dimension to the RHIC cable, which makes it easier to build a prototype magnet with minor modification to existing tooling. This was achieved by 1) reducing the twist pitch of RHIC type strand from 13mm to 4mm and 2) by introducing a 25μm core within the Rutherford cable. With this approach, the losses in the cable have been reduced by more than an order of magnitude and 16 km of tightly twisted strands of 6mm and 4mm twist was produced by industry. Measurements showed that the critical current and mechanical properties were minimally affected.

To reduce inter-strand ac losses in the cable, prototype 30-strand cable lengths were fabricated with several different core materials like stainless steel, anodized titanium, kapton and Nomex. The core raises the inter-strand resistance R_c between the upper and lower layers of the cable, and thereby reduces the eddy-currents induced in the cable when subject to rapidly changing magnetic fields. Inter-strand resistance measurements showed that cables made with Sn-4%Ag solder-coated strands with a stainless steel core had the best properties of low loss and good electrical stability. 600m of such a cable has been made by industry, which will be used in the first prototype magnet. However, the question of whether a magnet made from a high R_c cable can operate in a stable manner has yet to be established.

In FY 2002, we anticipate developing a small-filament ~ 2μm NbTi wire whose hysteresis loss would be half as much as the present 6 μm filament-diameter wire.

Magnet Testing: An existing magnet was tested twice at high ramp rate during this period to check the power supply operation, to study quenching as a function of ramp rate and maximum current, and to make a trial set of energy loss measurements. The magnet was a 3m long prototype, dual aperture magnet made with RHIC cable and insulation as part of the program to make magnets at BNL for LHC. Since it was built with RHIC cable and insulation, high losses and poor cooling were expected. Quench tests established that the magnet could be ramped at a high rate (1T/sec) without quenching, but intervals were required between successive cycles to prevent quenching due to conductor heating. This result will be used as a baseline when magnets with better cooling are tested during FY 2002. After considerable work on the power supply, a preliminary measurement of the eddy current energy loss was made (Fig. 1). Final measurements will be made after a final round of power supply improvements.

Magnet Construction: Surplus RHIC tooling is being modified for coil fabrication and magnet assembly. The design work for these modifications was nearly completed during FY 2001. Alternate cable insulation schemes were also studied. This is an important feature as the heat generated in the cable has to be conducted away rapidly into the helium. Two schemes have been proposed with one scheme being pursued by GSI, and another being developed at BNL.

Fixtures to test the turn-to-turn voltage integrity of cable made with insulation open along the edge were built and test procedures established.

In FY 2002, the first prototype magnet with core-cable will be assembled and tested. Testing methods at high ramp rates will be established and schemes to measure the field quality at high ramp rates will be explored.

SPECIFIC ACCOMPLISHMENTS:

Following are two refereed papers that will be published:

"Towards Fast Pulsed Superconducting Synchrotron Magnets" to be published in the proceedings of the Particle Accelerator Conference, 2001, (pre-FY 2001 work).

"Design Studies on Superconducting Cosθ Magnets for a Fast Pulsed Synchrotron" to be published in the proceedings of the 17th International Magnet Technology Conference, 2001, (includes new FY 2001 results).

LDRD FUNDING:

FY 2001	$143,588
FY 2002 (budgeted)	$145,000
FY 2003 (requested)	$156,000

Table 1. Losses/cycle calculated for a 3m RHIC dipole magnet at a dB/dt of 4T/s

Cable loss	Inter-strand Coupling loss (W)	2146
	Inter-filament Coupling loss (W)	217
	Magnetization Loss (W)	60
Iron loss	Iron magnetization loss (W)	27
	Iron Eddy current loss (W)	30
	Iron loss total (W)	57
Beam pipe loss	Loss in beam pipe (W)	32
	Total	2512

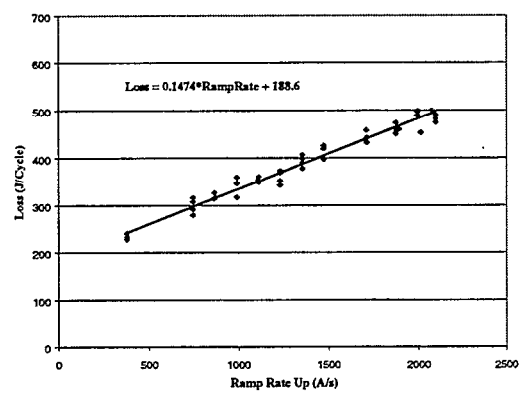


Figure 1: Loss per cycle versus average ramp rate.

Combination of Magnetic Fields and 20 keV Synchrotron X-rays to Produce Microbeams for Cell Culture Experiments

Louis A. Peña *01-11*

PURPOSE:

Recent biological experiments performed at the NSLS employing x-ray microbeams were problematic because the dose rates employed were many orders of magnitude beyond the scale of anything found in the established radiobiological literature. 8-20 keV photons have sufficient linear energy transfer to deposit most of their energy in several millimeters of water consistent with available cell culture configurations and desirable dose rates. However, at these energies the scattering of secondary emitted electrons threatens the sharpness of the microbeams -- sharp edges permit one to irradiate a row of cells while leaving the neighboring cells essentially unirradiated, while blurred edges result in intermediate doses to neighboring rows of cells, rendering certain kinds of experiments impossible to do. It is known that microbeams of ionizing radiation, particularly ionized particles, can have their path deflected by magnetic fields, but this has not been evaluated for x-rays to date. Thus, in practical terms, we hypothesized that a 2 T magnetic field could help to control the direction of secondary electrons to prevent blurring of the microbeam edges.

This modest LDRD supports a limited series of proof-of-principle experiments to test the effectiveness of combining magnetic fields with 20 keV x-rays, both in simulations and in actual practice with physical measurements and with living capillary endothelial cell cultures.

APPROACH:

We proposed to use a magnetic field to modify the dose deposition of electrons emitted from a low-energy polarized x-ray source due to the photoelectric interaction. An electromagnet with magnetic flux perpendicular to the direction of the photoelectron should be used to effect the electron transport. At the X15B beamline of the NSLS, a set of collimators, filters, and shutters are employed at to produce microscopically thin planar x-ray beams (1-100 μm thick) at energies ranging from 8-20 keV. An electromagnet tunable to 0, 1, and 2 T fields is placed downstream. A 2 cm aperture at the top of the magnet permits the introduction of materials into the beamline by means of stepping motors with 0.5 μm accuracy. Thus a controlled magnetic field can be applied to materials subjected to microbeam irradiation.

Two kinds of materials are irradiated for these studies: (1) MOSFET devices for physical microdosimetry measurements, and (2) capillary endothelial cell cultures grown specially modified plastic microscope "chamber slides" for a various biological endpoints. Both the offline MOSFET data analysis and biological work are done back in the Medical Department, Building 490.

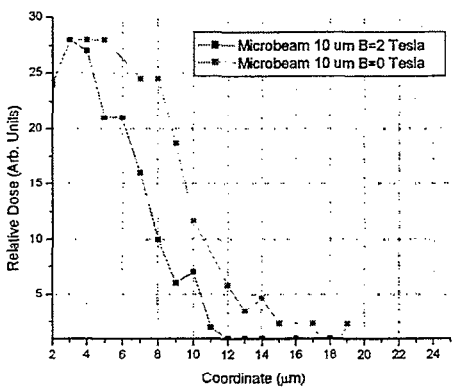
The EGS4 Monte Carlo code system is used to simulate physical parameters of microbeams, particularly low-energy polarized photon transport. Additionally, this code permits the researchers to control the photoelectron angular distribution in the simulation. User modifications were designed in order to parameterize the microbeam array size and spacing and to compare the absorbed dose profile with experimental MOSFET measurements.

The primary biological endpoint is identification of radiation-induced apoptosis

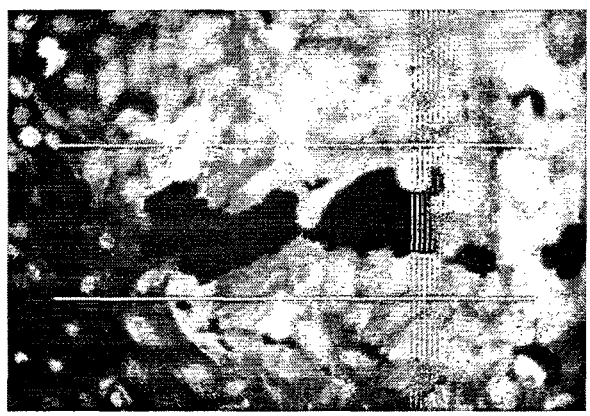
in situ by morphological criteria. Secondary endpoints include specific histochemical stains to visualize the cytoskeleton of neighboring non-irradiated cells and measurements of observable cellular changes versus microbeam with and/or deposited dose (0 - 100 Gy).

TECHNICAL PROGRESS AND RESULTS:

First, the utility of combining 2T magnetic fields with 8-20 keV x-ray microbeams was confirmed. The actual microdosimetery MOSFET measurements compared very well with Monte Carlo simulations, and demonstrated application of the magnetic field had the effect of sharpening the microbeam dose distribution. In the figure below, one such result demonstrates that at 8 keV, there is as much as a 3 μm difference. Applied to a target such an endothelial cell culture, this represents a very significant difference in the sharpness of the edges of the microbeams that penetrate the monolayer of cells.



Second, a series of radiobiological microbeam experiments with endothelial cell cultures demonstrated the feasibility of this technique. Image analysis of numbers of apoptotic cells per unit area of microbeam irradiated target are being done at the time of this writing. In this set of runs, we were able to visualize the cytoskeletal reorganization of surviving, unirradiated cells. A fluorescent dye conjugated to phalloidin intercalates with actin filaments revealing cytoskeletal organization. In the figure below, the path of a microbeam which transected this confluent monolayer of endothelial cells is indicated by white dotted lines. Between them, gaps in the cell monolayer are evident where irradiated cells died by apoptosis within 3 hrs. However, this figure shows that surviving cells immediately and dynamically fill the void and that their cytoskeletal filaments are all oriented perpendicular to the 30 μm wide microbeam.



SPECIFIC ACCOMPLISHMENTS:

None.

LDRD FUNDING:

FY 2001	$11,169
FY 2002 (budgeted)	$11,400

Gene Expression Profiling of Methamphetamine-Induced Toxicity in Neurons in Culture Using DNA Microarrays

Marcelo E. Vazquez *01-12*

PURPOSE:

Propose a method by which gene expression, as measured by cDNA microarrays, can be used as a highly sensitive and informative marker for toxicity induced by methamphetamine (METH).

Utilizing micro-array DNA chip technology, we propose to identify a specific set of genes in neuronal cultures that respond to METH for up to four weeks duration. Our hypothesis states that METH will have significant effects on neural functional integrity and cell survival. Therefore, the focus of our gene screens will concentrate on genes involved in apoptosis and signaling proteins. Intend to use microarrays as a tool for risk assessment that include genome-wide expression analyses to identify gene-expression networks and toxicant-specific signatures induced by METH (or other substance of abuse) that can be used to define mode of action, for exposure assessment, and for environmental monitoring.

Focus on the identification of the key regulatory genes that activate or repress or in some way regulate cascades or major circuits. Our goal is to identify: 1) which set of genes is a key regulator of the cellular response, and 2) whether modulation of the gene is possible, and 3) if it will result in an amelioration of the neurotoxic process.

This study will enhance our understanding of the molecular mechanisms of drug addiction and toxicity.

APPROACH:

Background: The cellular and molecular mechanisms involved in METH-induced neurotoxicity are not completely understood. The converging evidence indicates that METH redistributes dopamine (DA) from the reducing environment within synaptic vesicles to extravesicular oxidizing environments, thus generating oxygen radicals and reactive metabolites within DA neurons that may trigger selective terminal loss and cell death. Also, several reports indicated that METH treatment produces a modification in DA transporter function, which may be associated with both the altered uptake and release of DA. The observation that neuronal cell death and neuroplasticity involves an activation of gene expression and new protein synthesis, coupled with recent reports indicating that amphetamines are capable of immediately inducing early genes such as *c-fos, Zif*268 and *p*53, offers a possible clue as to their neurotoxic mechanism of action. However, the exact molecular and structural events involved in these changes have not been completely clarified. Thus, it is important to understand the patterns of oxidative stress-induced gene expression, which can provide valuable insight with respect to how free radicals-oxidative stress influences neuronal functional integrity. In addition, such information may provide new molecular targets for the development of countermeasures to ameliorate the toxic response.

Methods:

Neuronal cells (NT-2, hNT and hNT-dopaminergic type) are to be cultured on

multi-well plates, slide chamber-flasks or silicon windows, all pre-coated with attachment factors. Cultures are to be treated with graded doses of METH (0 to 500 μM/ml) and cells are to be harvested and/or processed at subsequent intervals (24, 48, 72, and 168 hours) for various biochemical, functional, and structural studies. Samples are to be processed to measure cell viability (Live and Death kits) using fluorescence microscopy, cell phenotyping (immunofluorescence microscopy and western blot), structural integrity using soft x-ray microscopy and live images that are to be recorded for neurite outgrowth quantification using an image analysis algorithm developed for this project.

For gene expression studies, mRNA are to be isolated with the Micro-FastTrack 2.0 mRNA isolation kit (Invitrogen Corp.), following lysis of the cells directly on the dishes. Subsequent steps are to be performed according to the kit manufacturer's protocols. Total isolated RNA from cultures are to be frozen for shipment to SUNYSB. One microgram of mRNA will be used for making fluorescent-labeled cDNA probes for hybridizing to the 5K or 40K microarrays on glass slides. Hybridization, washes and fluorescent scans will be performed at SUNYSB. The ScanAlyze program will be used for gridding and quantitation of scanned microarray images.

Collaborators:

Core Project: Marcelo E. Vazquez, PI, Gaofeng Fan, Luis Estevez, Jeanine Thomas
DNA Microarrays: Anilkumar Dhundale, Center for Biotechnology at SUNYSB.
Soft X-ray Imaging: Carolyn Larabell, Advanced Light Source at Lawrence Berkeley National Laboratory.
Image Analysis: Christina Wilson, Applied Mathematics and Statistics at SUNY Stony Brook, and BNL CDIC. Brent Lindquist, Applied Mathematics and Statistics at SUNY Stony Brook.

TECHNICAL PROGRESS AND RESULTS:

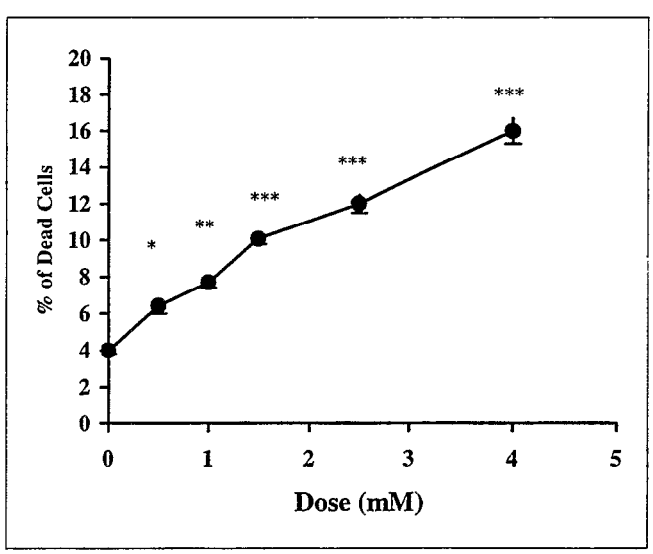
Made substantial progress in characterizing several cellular models to study the cellular and molecular effects of METH in cultures, as well as set up and tested several techniques to delineate the relationships between the multiple endpoints associated with METH-induced toxicity.

Several NT-2 clones were purchased from Stratagene. Each of these clones were expanded to mass population, aliquoted and placed under liquid nitrogen until needed. In addition, several aliquotes of fully differentiated hNT neurons have been generated by treating NT-2 cells with retinoic acid, aliquoted and stored for future use. In addition, NT2 cells were induced to differentiate a dopaminergic phenotype by treating the cells with lithium chloride and retinoic acid (RA), allowing its use as a human dopaminergic cell line for toxicological studies. In order to confirm the dopaminergic phenotype of this modified hNT cells, two methods were employed: western blots and immunocytochemistry to detect the expression of dopaminergic markers such as tyrosine hydroxylase, dopamine, dopamine transporter and receptors.

In order to evaluate the toxicity of METH in vitro, a battery of techniques to quantify cell survival and apoptosis were tested. Biochemical methods (MTT) and flow cytometry were compared with the fluorometric assays. After several trials, it was determined that the Live Cell/Dead

assay was the most sensitive, reliable, cheap, and accurate method to measure METH-induced cell toxicity. Utilizing ethidium hemodimer and calcein-AM, we were able to achieve good discrimination between dead (red) and viable (green) cells after 15-min incubation at 37°C. The methods were tested by treating hNT cells with graded acute doses of METH in culture. Samples were fixed at different time points to study dose- and time-dependence for cell damage.

Established and characterized the cellular effects of METH exposures on dopaminergic-like cells in culture, providing the necessary "ranging" data to determine in vitro cellular and molecular effects of METH. Determined cell survival and phenotypic changes for hNT cells exposed to METH as a function of dose and post-treatment time. Selected a specific dose and time point for microarray sampling. For the assessment of viability, the cells were plated on poly-L-lysine coated slide chambers (LabTek) at a density of 50.000 cells per chamber and treated with various concentrations of METH. Cells were harvested at 24, 48, 72, and 168h after exposure to METH (Only 24 h data is presented below, additional dose points are currently being analyzed).

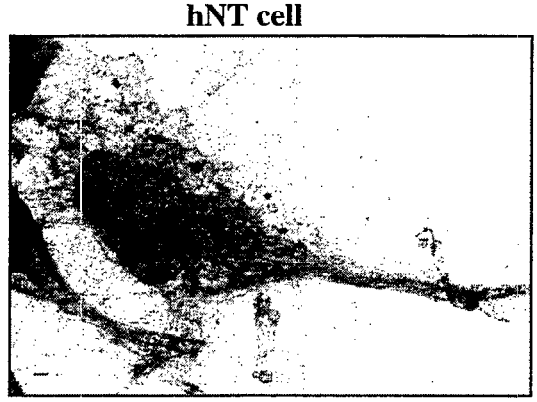


Results show that METH induced a dose-dependant toxic response on hNT-dopaminergic cells. Doses as low as 0.5 to 1 mM/mL produced dead cells as well as morphological effects such as membrane blebbing, neurite degeneration and vacuolization.

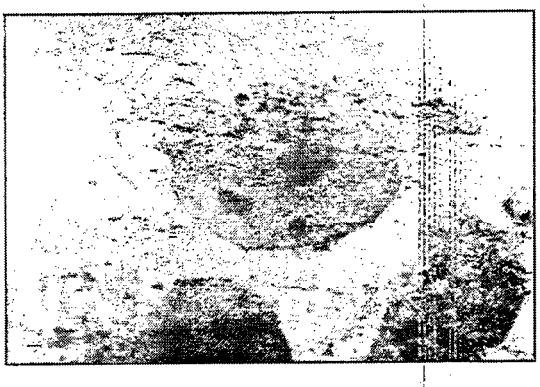
Samples of METH-treated NT-2 and hNT cells were harvested for DNA microarray processing a Micro-FastTrack 2.0 kit (Invitrogen Corp.) was employed to isolate mRNA, following lysis of the cells directly on the flask chambers. Samples tested showed a high degree of integrity, allowing a test of the sampling procedures before the shipment for microarray processing.

The high-resolution soft x-ray microscope (XM-1) at the LBNL Advanced Light Source was used to examine whole, hydrated cultured neuronal cells. Using x-ray microscopy, high contrast information about the organization of the cytoplasm and nucleus of these cells were revealed at unsurpassed resolution (36 nm) (five times better) than possible with visible light microscopy. Several images were taken from chemically foxed untreated cultures demonstrating that high-resolution images can be obtained for structural analysis. Both NT2 and hNT cells revealed excellent ultrastructural details of the cell nucleus and cytoplasm as shown in the figures below.

hNT cell



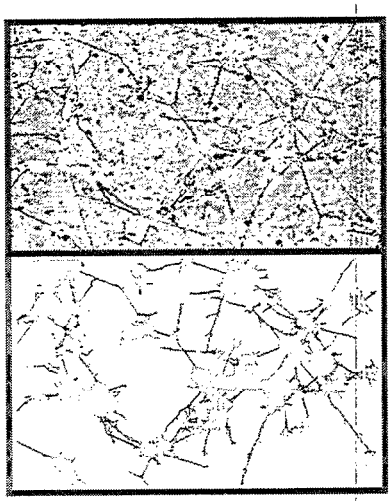
NT2 cluster



In order to quantify the effect of METH on neuronal terminals or neurites (neuronal processes), images from an experimental series were captured and analyzed. We were able to observe the neurite outgrowth from neurons treated with METH in culture and to quantify the extent of growth as a marker of functional integrity.

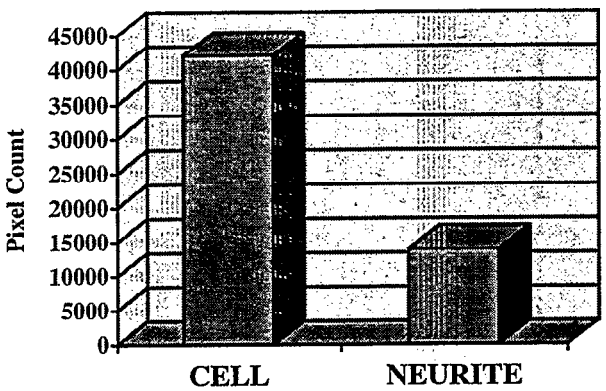
Adapted algorithms developd to reconstruct and quantitate neurite outgrowth from retinal explants and applied them for disassociated cells such as NT2 and hNT. The final result is the measure of cell body and neurite total mass expressed as pixel count (see figures).

hNT cells original image



hNT cells reconstructed image

Quantitation of neurite outgrowth



These imaging techniques are of critical importance in determining the relationships between a set of genes-gene products, structural changes and functional changes induced by METH. Results obtained from these investigations may elucidate important pathways linking patterns of early gene expression to more permanent and persistent changes in gene expression which contribute to the toxic effects of METH.

SPECIFIC ACCOMPLISHMENTS:

Presentation: Review of LDRD FY 01 Approved Projects, Berkner Hall, March 19, 2001.

LDRD FUNDING:

FY 2001	$105,192
FY 2002 (budgeted)	$ 99,800

Functional Spectral Signature (FSS) Method for the S/N Enhancement of Brain Patterns in PET Images

Christoph Felder *01-13*

PURPOSE:

Develop a methodology to detect and quantitate faint group-specific patterns of differences in functional activity of brain images by improving the signal-to-noise (S/N) ratio without blurring images as conventional methods do. The reason for doing so is the inherent problem of anatomical and functional variability among subjects. Unfortunately, this requires the use of blurring filters with full widths at half maxima (FWHM) that are much larger than typical Positron Emission Tomography (PET) scanner resolutions. There are no good criteria to determine a-priori what FWHM should be used. Actually, optimal values vary for different brain regions and studies. Methods that avoid blurring to increase the S/N ratio are highly desirable as they give more accurate values for statistical quantities, which in turn means that the same accuracy can be obtained with smaller group sizes. Obviously, this results in a reduction of costs or time needed to carry out a study. In addition, much more precise information can be obtained with respect to activation size and exact locations of changes that occur in each individual.

APPROACH:

As has become evident from MR- and high-resolution PET scanners, responses to a task or challenge do indeed occur in different sub-structures in different people. Due to these limitations in co-registration accuracy, conventional methods apply (Gaussian) smoothing kernels to the brain images with values for the FWHM of 12-16 mm or even more before statistical inferences are made. Our newly developed Functional Spectral Signature (FSS) methodology abandons the concept of smoothing or blurring of images by determining the shifts or deformations to be applied locally at the sites of potential interest, called land-marks, in order to align functional activation foci. In contrast to existing methods in which the *non-linear* co-registration and the statistical inferences (after smoothing) are two separate steps, the FSS method expresses the objective function used to determine local deformations directly in terms of the statistical parameter t.

More specifically, this iterative approach is performed in the vicinities of group-specific local changes in activation, or land-marks, by determining for each subject in sequential order the amount by which its image has to be locally shifted in 3 orthogonal directions until the t-value at the position of the land-mark reaches a maximum. Once the shifts for each subject are determined in this way the procedure is repeated until the new shifts become smaller than 1 voxel. For most practical purposes it is enough to compute an initial t-map and to use the local maxima as land-marks. Hence, the land-marks are obtained in an automatic fashion, and then the FSS method focuses directly on the potentially interesting sites (which also reduces computing time).

TECHNICAL PROGRESS AND RESULTS:

The FSS method was developed by means of a simulation study beginning in FY2001 as reported in the mid-year review and was successfully expanded from 1 dimension to 3 dimensions. For practical purposes the figures attached below show the results in 2 dimensions (with signal intensities as 3rd

dimension). The simulation program for the FSS method was implemented using the PV-WAVE software for image display and has been partially written in C to improve the speed in future applications on real data. The simulation was designed to be as realistic as possible and contains the following components:

Activation signals. The signals representing activations with respect to baseline are generated for any chosen number of subjects as Gaussian curves with an FWHM of 6.5 mm, the resolution of the older of the 2 PET scanners used at BNL. Thus, the signals represent the smallest possible extent size that can be detected. For the figures below five such subject signals per group with intensities evenly distributed between 0.5 and 1.0 were simulated such that the response varies within a factor of two.

Signal spread. The individual signals within a group are displaced within a selectable range. Three groups of signals with a spread of 0, 10, and 20 mm (maximum anatomical variability in cortical areas) within a group were used for the figures shown below.

Random noise. White random Gaussian noise with a mean of 0 and a standard deviation of 1 was generated. Like the activation signals the noise was smoothed by a Gaussian kernel of 6.5 mm FWHM which reduces the standard deviation to about 0.11. However, the noise can be scaled by any factor to simulate the desired S/N ratio. Typically a scaling factor of 1.2 was applied such that amplitude between positive and negative standard deviation amounts to about half of the lowest signal intensity. While neither the PET resolution is strictly uniform nor the actual noise normally distributed (because they are affected by the acquisition mode, the count rate, the reconstruction algorithm employed, as well as scatter and other correction factors) the noise simulated in this way was still considered to be the best approximation, and it shall simply reflect the highest noise level over the entire image that can be dealt with.

Based on these tools a wide range of S/N ratios and signal spreads could be simulated. Figure 1 illustrates an example of 3 groups of 5 signals each as described above. The groups are identical with the exception of the inter-signal spread of 0, 10, and 20 mm. Finally, Figure 2 summarizes the results obtained by the FSS method. It is demonstrated that the FSS method finds the exact positions and the correct t-values. Moreover, the exact position of each *individual* signal is known after using the FSS method whereas no such information is obtained when conventional smoothing methods are applied.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2001	$85,941
FY 2002 (budgeted)	$86,100

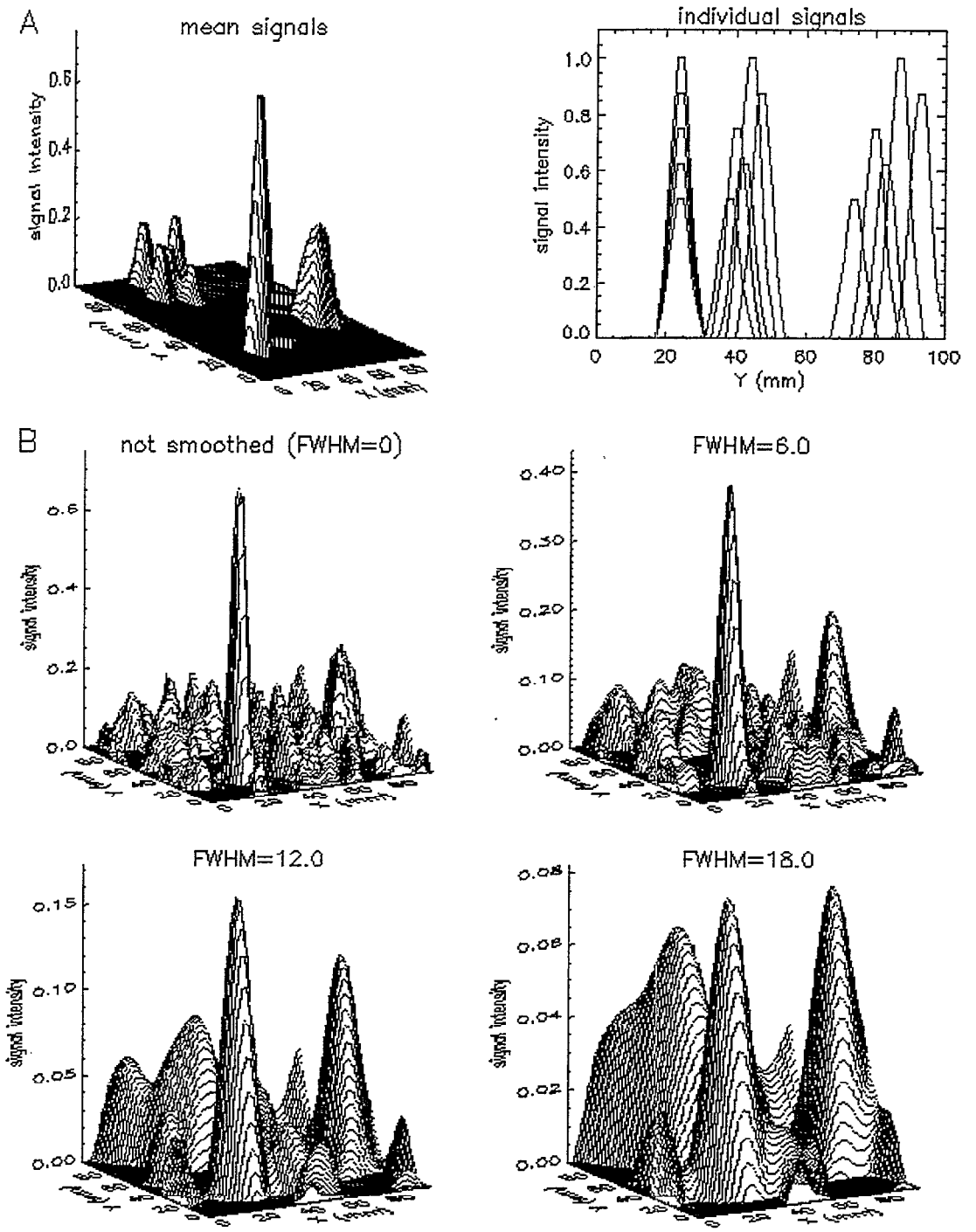


Figure 1 Three groups of 5 Gaussian signals with intensities between 0.5 and 1.0, having an inter-signal spread of 0 (lowest Y), 10 and 20 mm (highest Y). A) group averages (left) and individual signals projected onto Y (right) in the absence of noise. B) Group averages in the presence of white Gaussian random noise of zero mean and a standard deviation of 0.11after smoothing with a Gaussian kernel using FWHM values of 0, 6, 12 and 18 mm. Without smoothing the group mean is barely visible for an inter-signal spread of 10 mm and is completely lost for a spread of 20 mm. Smoothing enhances the S/N ratio at the cost of localization. The higher the signal spread the higher a FWHM is necessary to detect an activation.

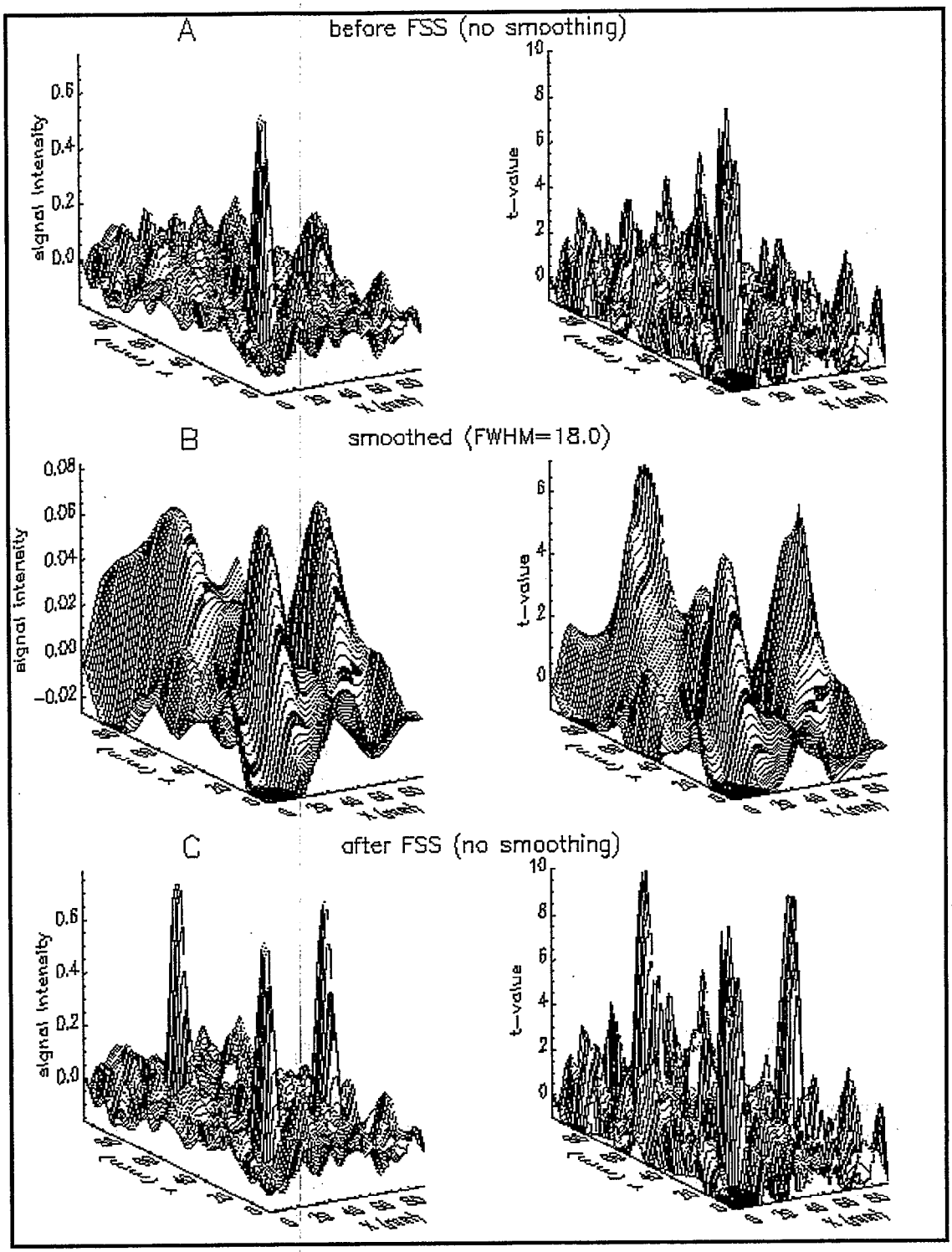


Figure 2. Mean signal intensities (left) and t-value distributions (right) of the 3 groups shown in Figure 1 in the presence of noise. A) without any S/N enhancement. B) S/N enhancement by smoothing the individual images with a FWHM of 18 mm. C) S/N enhancement obtained by the FSS method. t-values are improved over the smoothed ones and the method can completely correct for the initial inter-signal spread. The exact location of each signal maximum position is obtained whereas no such information is available when using standard smoothing filter methods.

Exploration and Development of Ultrafast Single Shot Detection Methods For Use with Pulse Radiolysis Experiments at LEAF

Andrew R. Cook *01-18*
J. Miller

PURPOSE:

This project was established to explore new detection methods that can be used to study chemical problems at the Laser Electron Accelerator Facility (LEAF) in the Chemistry Department's Center for Radiation Chemistry (CRCR). While pulse radiolysis is a very powerful tool for the study of many chemical systems, there are two main problems that we hope to solve. These include the large amount of time that can be required to collect transient data in repetitive variably delayed electron pulse - laser probe experiments on faster timescales and the fact that radiation chemistry techniques often cause the degradation of samples and buildup of ionization products. As photocathode accelerators have opened new fields of chemical studies, the development of single shot detection methods for fast timescales have the potential to not only accelerate current studies, but enable whole new areas of study. In particular, where synthetic samples are often of the greatest interest and are available only in small quantities. Success would lead to dramatic contributions to DOE programs in diverse areas such as photochemical energy conversion and molecular electronics/nanotechnology and would help propel LEAF to the status as the world's premier facility for accelerator based chemistry.

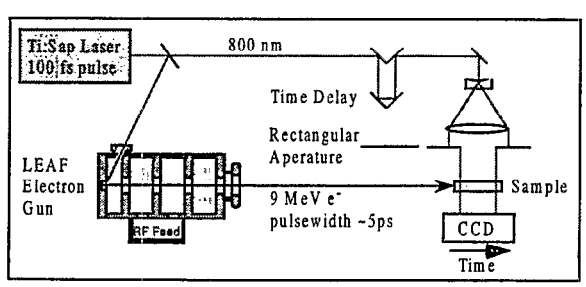
APPROACH:

The basis for ultrafast single shot detection is spatial encoding of temporal information. Related methods are currently used for the measurement of ultrafast laser pulse widths and were recently applied for the first time at MIT to ultrafast time resolved spectroscopy for the study of irreversible reactions in solids. Such methods have never been applied to accelerator based chemistry problems. Temporal information can be encoded in a variety of ways across a laser beam, and be read out by collecting a snapshot of the transverse profile of the beam on a CCD camera. The goals for this first year's work were: 1) identify and hire a postdoctoral associate; 2) purchase off the shelf and custom components, assemble and test hardware, and begin developing data collection and analysis software to demonstrate the feasibility of the concept with the simplest possible experimental arrangement.

TECHNICAL PROGRESS AND RESULTS:

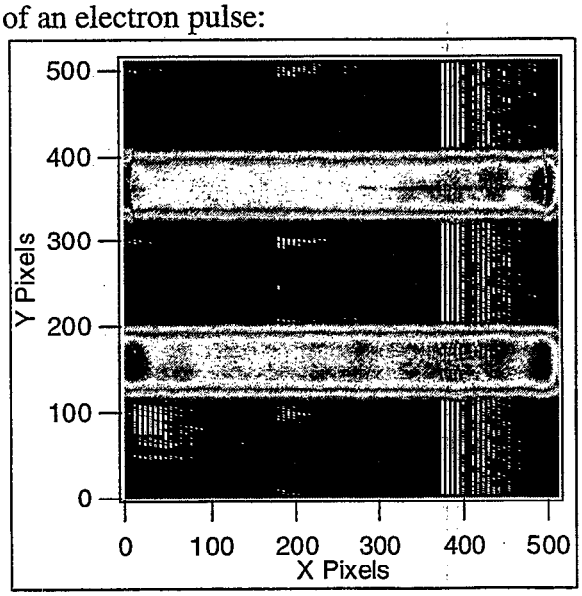
A postdoctoral associate, Zhen Hui Zhang, was hired on 6/4/01, and has begun to aid in our efforts.

The work this year proceeded in two phases. In the first phase, an experiment was set up where the laser and electron beams crossed in a sample at 90°. In this arrangement, the relative time at which the pulses reach the sample varies linearly with displacement along the path of the electron beam:

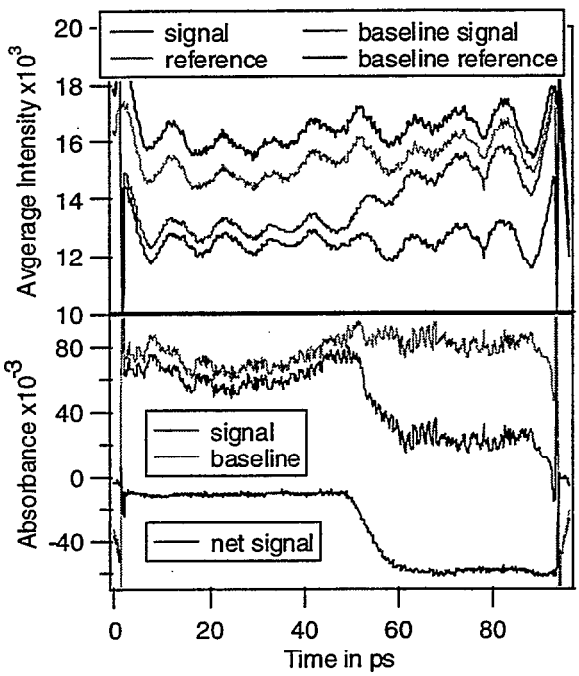


While the data were poor quality and authentic signal may not have been observed, some of the most significant factors affecting success were identified. These included the importance of preparing and maintaining the highest quality transverse profile of the laser beam, eliminating interference effects, the effect of shot-to-shot changes in the spatial profile and intensity of the laser, and a better understanding of the obtainable time resolution as a function of sample dimensions and imaging on the camera.

Leveraging what we learned, we designed, built, and tested the considerably more complicated second-phase experiment in this project. This involved very careful generation of a uniform rectangular profile laser probe beam, the addition of a second beam split off from the first to use as a reference, upgrades to our CCD camera controller, software, and modifications to the camera head, imaging of the sample on the CCD camera, and software written to process the data collected. In this process an important technical issue was identified: at all times, exceptional care was required to avoid interference effects due to edges and defects in the optics. We tested the system using optical excitation of a laser dye instead of an electron pulse:



The stripes in this figure are the transverse profiles of the probe signal and reference beams. A second image was also collected without the pump beam to provide baseline information. Since all vertical points in a stripe are at the same time, they can be averaged. Once this is done for all four of the stripes (top panel), the sample absorbance as a function of time can be determined (bottom panel):



The net signal is a bleach in the laser dye absorption at 800nm, with a rise time of about 7-8ps as expected from the experimental geometry used. This rather exciting result demonstrates not only the feasibility of ultrafast single shot detection methods, but exceeded our expectations in the quality of data obtained. The apparent noise level in the net signal above, *collected with a single laser shot*, rivals that obtainable in existing pulse-probe experiments which require on the order of 10^4 shots to collect. With automation, this not only preserves high value limited quantity samples, but also can reduce data collection times from more than an hour to less than one minute!

Future work in the second year will focus in two areas. First, more effort will need to be spent understanding all of the parameters involved in the collection of high quality data, and additional hardware needs to be installed and software written to automate data collection and analysis. First, data will be collected looking at processes following pulse radiolysis showing the ability to use LEAF's full-time resolution of 5-7 ps. Second, alternative methods of introducing delay will be investigated. Weaknesses of the method used above are limited time resolution and limited width of the time window. Other methods like using "stair-stepped" optical echelons can improve time resolution towards 100-200 fs for certain types of experiments, while bundles of various length fibers may be used to provide very long total time windows extending out into the nanosecond range, while still maintaining a 5-7 ps time resolution.

SPECIFIC ACCOMPLISHMENTS:

No publications or patents at this time.

LDRD FUNDING:

FY 2001	$62,401
FY 2002 (budgeted)	$65,000
FY 2003 (requested)	$65,000

Metal Nanoclusters and Electron Transfer in One, Two, and Three Dimensions

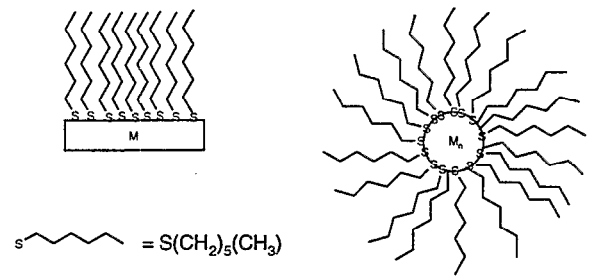
Carol Creutz *01-19*

PURPOSE:

The purpose of this work is to perform research in the reactivity and properties of nanoscale metal clusters, which are of great interest for their novel properties and possible applications. The nano clusters will be used to characterize, model and control electron transfer reactions involving molecular and nanoparticle partners in order to advance the design and construction of "molecularly wired," nano-scale devices. An initial goal is to explore and understand the interaction of excited states of transition-metal complexes with metal nanoclusters as a function of cluster size. This project is a component of the BNL nanoscience initiative and the proposed *Brookhaven Center for Functional Nanomaterials.*

APPROACH:

Monolayer Protected Cluster Molecules ("MPCs", e.g. $Au_{145}(S(CH_2)_5(CH_3)_{50})$ are isolable, alkanethiolate-protected gold clusters of 5-nm core diameter. Since 1994, with the publication of a new synthetic method inspired by recent work on self-assembled monolayers on surfaces, research exploiting the novel properties of these nanometer scale metal clusters/crystals enveloped by a structured layer of organic molecules has exploded. Phosphine-capped gold clusters in the 0.5 to 3.0 nm range, e.g. $Au_{101}[P(C_6H_5)_3]_{21}Cl_3$ exhibit similar properties and provide useful starting materials for construction of clusters of specific size. Larger clusters from citrate-based colloidal gold preparations will also be of interest.



Left: Self-assembled monolayer (SAM) of 6-carbon thiolate, $S(CH_2)_5(CH_3)$, on (bulk) metal M surface
Right: Monolayer protected cluster (MPC) of the same thiolate on M_n,a nanocluster of metal M

Electron donors and acceptors will be covalently or electrostatically attached to the same or to different clusters and the effect of the size, charge state, and nature of the clusters and tethers on thermal and photo-induced charge-transfer processes will be examined. Electron transfer in solution will be probed by fast transient methods; on surfaces, by scanning tunneling microscopy and other methods to be developed in collaboration with J. Warren, BNL Instrumentation Division. Research Associate Dr. Janet Petroski started experimental work in March 2001 and is responsible for the results reported here.

TECHNICAL PROGRESS AND RESULTS:

The gold clusters synthesized in FY 2001 are summarized in Table 1. Their absorption spectra are presented in Figure 1. The clusters were characterized by NMR (^1H and ^{31}P) to verify incorporation of the desired organic cap and by electronic absorption spectroscopy, which provides some size information through the presence or absence of the gold plasmon band. However, verification of their sizes and size distributions was essentially impossible until 11/01 because of lack of access to transmission electron microscopy (TEM).

The JEOL 100CXII has now been rebuilt and is providing highly needed TEM characterization for a number of new nanoscience projects. TEMs for large clusters (G, Table 1) and much smaller phosphine-capped clusters (B, Table 1) are presented in Figure 2.

In FY 2002 the applicability of scanning probe microscopy to characterization of the nanoclusters will be investigated. Improved methods for synthesis and purification of the clusters will be sought and charge transfer processes of the clusters will be probed. Charge injection into the clusters will be studied as a function of cluster size/electronic structure and capping material. We gratefully acknowledge the assistance and cooperation of B. Panessa-Warren and C. Czjakowski in making the TEM measurements possible.

SPECIFIC ACCOMPLISHMENTS:

BES-Chemical Sciences Nanoscience and Technology Award FY01 - 04 $650K/year.

LDRD FUNDING:

FY 2001	$ 81,202
FY 2002 (budgeted)	$145,000
FY 2003 (requested)	$145,000

Table 1. Summary of Clusters Synthesized

Sample	Size (nm)	Starting Material	Solvent	Capping Material	Reducing Agent	λ_{max} (nm)
A[1]	0.5	AuCl	CH_3OH	PR_3[7]	$NaBH_4$	280, 316, 420
B[2]	1.5	$HAuCl_4$	Toluene or CH_2Cl_2	$P(C_6H_5)_3$	$NaBH_4$	none
C[3]	3	$HAuCl_4$	Toluene	$(C_7H_{15})_4NBr$	$NaBH_4$	524
D[4]	9	$HAuCl_4$	H_2O	Citrate	Citrate	518
E[4]	15	$HAuCl_4$	H_2O	Citrate	Citrate	520
F[5]	15	$HAuCl_4$	H_2O	$HS(CH_2)_2SO_3H$ and citrate	Citrate	520
G[4]	22	$HAuCl_4$	H_2O	Citrate	Citrate	522

References for Table 1:

1. Hainfeld, J. F.; Liu, W.; Barcena, M. *J. Struct. Biol.* **1999**, 127, 120.
2. Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E. *J. Am. Chem. Soc.* **2000**, 122, 12890.
3. Fink, J.; Kiely, C. J.; Bethell, D.; Schiffrin, D. J. *Chem. Mater.* **1998**, 10, 922.
4. Enüstün, B. V.; Turkevich, J. *J. Am. Chem. Soc.* **1963**, 85, 3317.
5. Kim, Y.; Johnson, R. C.; Hupp, J. T. *Nano Lett.* **2001**, 1, 165.
7. 3,3',3"-Phosphinodyne tris(benzenesulfonic acid) trisodium salt and 4(Diphenylphosphino)benzoic acid

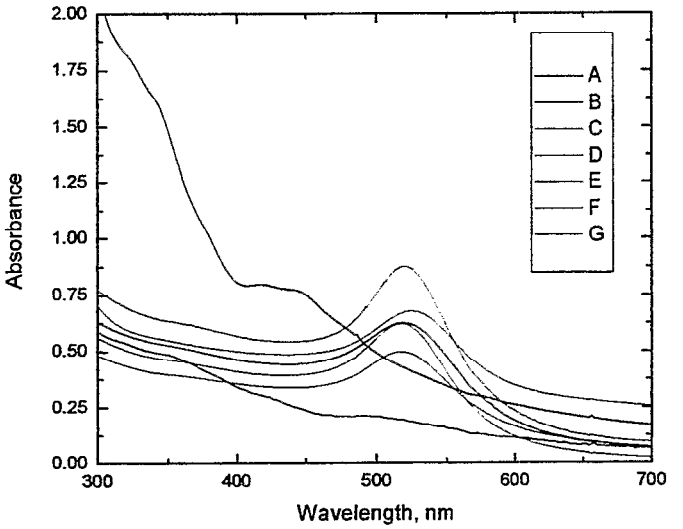


Figure 1. UV-visible absorption spectra of the clusters summarized in Table 1. The ca. 520 nm absorption band seen for C through G is the gold plasmon band, absent for smaller A and B clusters (Table 1). Cluster A exhibits molecular orbital based absorptions characteristic of the Au_{11} cluster.

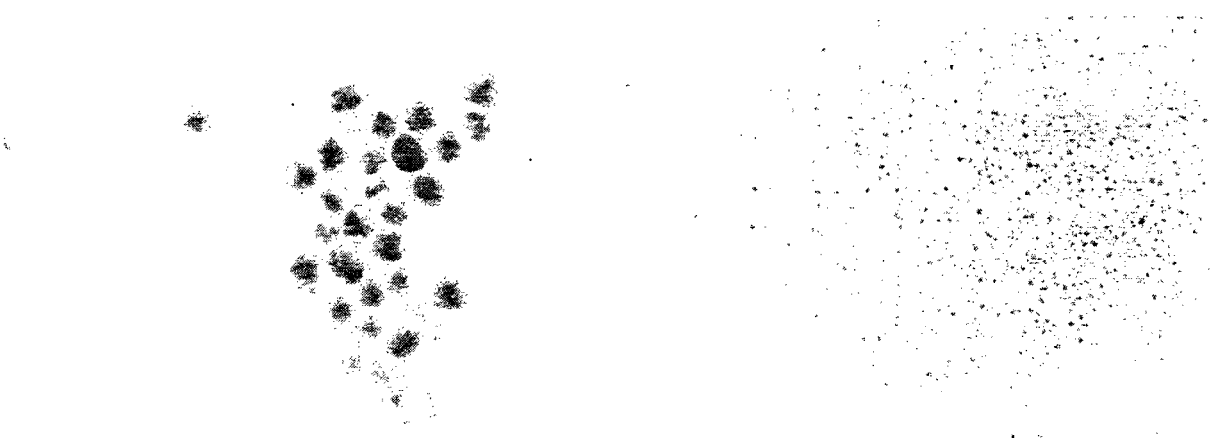


Figure 2. Transmission electron micrographs of "22 nm" (left, G in Table 1) and "1.5 nm" (right, B in Table 1) gold clusters at 270,000 and 320,000 magnification, respectively. The gold core is imaged, but the organic capping material is not.

Molecular Wires for Energy Conversion and Nano-Electronics

John Miller *01-20*

PURPOSE:

Examine molecules that may act as molecular wires to learn about their 1) energy levels, 2) changes in optical spectra upon addition of an electron or a hole, 3) transport properties for movement of electrons and holes, 4) effect of stray charges (e.g. Na^+) on the transport and spectra. A beginning goal is to determine applicability of the new techniques proposed to obtain answers to these questions.

APPROACH:

Interest in molecular electronics has led to an explosion of interest in "molecular wires," molecules of nanoscale lengths that are capable of transporting electronic charge. The premises of our approach are that such wires would have applications to energy capture and storage as well as to electronics, and that special insight could be gained from the use of BNL's new Laser Electron Accelerator Facility (LEAF).

Much information about transport properties can be gained from spectra. While there are many chemical methods to obtain such spectra, LEAF can obtain them in situations where they can not be produced chemically. These situations include production in media incompatible with strong redox reagents necessary to add charges to the wires, or in weak or non-polar media or in such media in the presence of inert counter-ions that may trap the electronic charge.

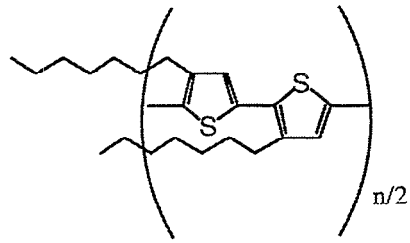
The second advantage to LEAF experiments is the potential for high-time resolution. Investigators in other laboratories have attached molecules to electrodes and measured current-voltage characteristics. Such experiments are rich in information, but have very low time resolution. Further attachment of the wires to the electrodes is difficult to accomplish and it is more difficult to know what has been attached-how many wires, and in what configuration. At LEAF it may be possible to observe the movement of charge in molecular wires in a direct, time-resolved way.

The LEAF experiments have their own difficulties to be overcome. One of these is getting sufficient material into solution to enable it to capture charges quickly. It is necessary to obtain appropriate materials and find appropriate solvents. We recently received an interesting material from Tianbo Liu (BNL Physics) that may be helpful in this regard.

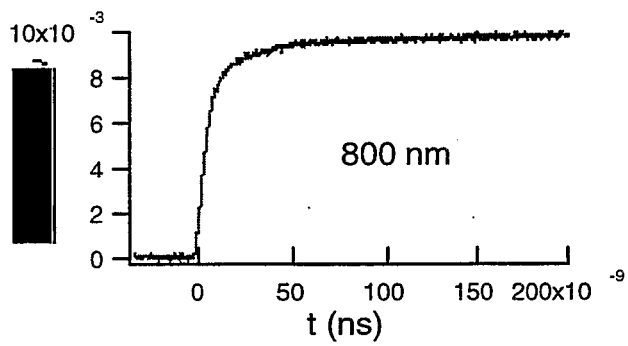
TECHNICAL PROGRESS AND RESULTS:

Post doctoral research associate Dr. Norihiko Takeda joined us in April. Dr. Takeda has become familiar with use of the LEAF accelerator and begun experiments. Because one of the principal hurdles is getting material into solution he has performed tests on solubilities of materials in several solvents. Satisfactory results were obtained in only a few cases.

Transient absorption was observed after electron attachment to alkylated (for solubility) polythiophene:



A transient spectrum was observed showing a small, broad band in the near infrared at 1600 nm and a much stronger one at 800 nm, both of which had a long lifetime after creation by a pulse from LEAF. A kinetic trace at 800 nm is shown below, which represents an electron within the "wire."



In the coming year spectral data from this and other molecules will be compared to seek information about relationships between the spectra and transport properties. A strategy has been developed to "dope" the wires with charge traps at low densities (e.g. 1 dopant/100 repeat units). Experiments will seek conditions in which the doping strategy can successfully determine transport within the wire.

SPECIFIC ACCOMPLISHMENTS:

No publications or patents, yet.

LDRD FUNDING:

FY 2001	$47,655
FY 2002 (budgeted)	$50,000
FY 2003 (requested)	$51,000

Nanoscale Catalysts: Preparation, Structure and Reactivity

Jan Hrbek *01-21*
J.A. Rodriguez

PURPOSE:

Mo based oxide and sulfide catalysts are widely used in the chemical and petroleum refining industries. By far their most important application involves hydro-desulfurization processes, where sulfur-containing molecules are removed from petroleum by reaction with hydrogen to form H_2S and hydrocarbons. New environmental regulations emphasize the importance of more efficient technologies for removing the sulfur from the oil. This fact has motivated a search for novel catalytic materials that can accomplish such a task. Our goal is to prepare Mo nanocatalysts that have a narrow range o sizes and high activity.

APPROACH:

The clean Au(111) surface exhibits a long-range reconstruction usually referred to as herringbone structure. It has been shown that this herringbone structure can be used as a template for adsorption and direct growth of metal nanoclusters that have a narrow size distribution. Our approach involves the use of the Au(111) surface as a template for growing MoS_x, MoO_x and MoC_x nanocatalysts using $Mo(CO)_6$ and other molecular precursors (S_2, NO_2, C_2H_4). The structure and morphology of the formed nanoparticles will be examined by means of scanning tunneling microscopy (STM), whereas photoemission at the NSLS will be the main tool for characterizing the chemical properties.

TECHNICAL PROGRESS AND RESULTS:

In FY2001, our experiments at the NSLS demonstrated that MoS_x aggregates can be prepared from the reaction of $Mo(CO)_6$ and S_2 on a Au(111) substrate. The formed MoS_x nanoparticles were more reactive towards thiophene than extended $MoS_2(0002)$ surfaces, MoS_x films, or MoS_x/Al_2O_3 catalysts. This could be a consequence of special adsorption sites and/or distinctive electronic properties that favor bonding interactions with sulfur-containing molecules. In addition, different approaches were tested for the synthesis of MoO_x and MoC_x nanoparticles on Au(111).

In the coming year, we plan to perfect our procedure for the synthesis of MoO_x and MoC_x nanoparticles. Using scanning tunneling microscopy, we will investigate in detail the effects of size on the chemical reactivity of these systems. Theoretical calculations will be performed to explore links between their electronic and chemical properties.

SPECIFIC ACCOMPLISHMENTS:

One paper, Formation of Mo and MoSx nanoparticles on Au(111) from Mo(CO)6 and S2 Precursors: Electronic and Chemical Properties, has been published (Rodriguez et al, Surf. Sci. 490 (2001) 315), and a second one is being written to be submitted before the end of this year.

LDRD FUNDING:

FY 2001	$76,395
FY 2002 (budgeted)	$80,000
FY 2003 (requested)	$80,000

Experimental and Theoretical Studies of the Formation of Titanium-Carbon Nanoclusters

Trevor J. Sears *01-23*
G. E. Hall
J. T. Muckerman

PURPOSE:

Focuses on a fundamental understanding of the structure, formation, and reactivity of small metal-containing cluster species. These are precursors to nanocrystalline materials that have many potential applications, including highly specific and efficient catalysts for industry. The effort incorporates both experimental and theoretical approaches with the former directed towards high precision measurements of cluster properties that will validate high-level *ab initio* calculations of the properties of small cluster compounds. These in turn will serve as benchmarks for future semi-empirical approaches to calculations on larger nano-crystalline materials where rigorous methods are not applicable. The work forms part of the nanocatalysis initiative within the Chemistry Department and BNL.

APPROACH:

There has recently been much interest in the properties and reactivity of metallo-carbohedrene or met-car clusters which were originally discovered in 1992 in the form of positive ions of the type $M_8C_{12}^+$, where M is a transition metal atom. Intially, interest centered on the unusual stability of these species and, by analogy to fullerenes, this is assumed to be related to a highly symmetric cage-like structure. However, there is more than academic interest in such species because many have been shown to possess chemical or physical properties that have important industrial and economic consequences.

For example, titanium-containing carbon films form very hard and wear-resistant coatings, a property thought to be derived from nano-crystalline TiC embedded in a carbon matrix. Other carbides, for example MoC, show great promise as potential catalysts for methane reforming and fuel desulfurization.

The rational design of future materials depends upon a fundamental knowledge of the basic principles that underlie correlations between the electronic and geometrical structure of the nanoparticles and their physical and chemical properties. Understanding the reactivity and stability of a coordinatively unsaturated metal atom in an active catalytic site, for example, must necessarily involve a *molecular* description of the chemical bonding and electronic wavefunctions.

In this program, we have designed and constructed an experimental apparatus for the production of small metal-containing species that are subsequently studied using high-resolution optical probes. Samples of the molecular clusters can be deposited downstream of the gas phase spectroscopic experiments and subsequently characterized by microscopic and X-ray techniques. These experiments yield very precise information on the electronic structures of the molecular clusters and correlate specific gas phase chemistry with resultant film or bulk crystalline structures.

In parallel, we have developed computational techniques that can accurately reproduce the measured electronic and structural properties of the molecular species. The aim is to understand and validate the approximations that can be made to increase computational efficiency

without compromising the accuracy of the calculation. Such knowledge is essential for future application of numerical methods to larger or bulk crystalline materials where high-level *ab initio* calculations are impractical.

TECHNICAL PROGRESS AND RESULTS:

We have designed and constructed a new experimental apparatus for the production of molecular beams of metal-containing species. A photograph is shown in Fig. 1.

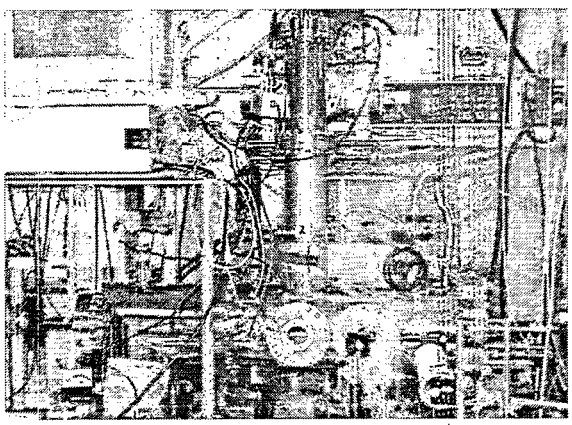


Figure 1. Photograph of experimental chamber. The laser ablation source is on the right, and the molecular beam travels from left to right. The time-of-flight mass spectrometer extends upwards from the second section of the chamber after the skimmer.

The species of interest are formed by laser ablation of the target metal followed by chemical reaction with a reagent seeded in low concentration in a supersonic rare gas expansion. Other transient photochemical or pyrolytic production methods may also be used, depending on the species under study. The cluster sample can be probed by various laser beams, both before and after a skimmer that separates the source chamber from a differentially pumped second section where photoionization followed by time-of-flight mass spectrometry is used to characterize the species distributions. Finally, sample slides may be inserted to intercept the beam at a downstream position where chemical reactions have completed for subsequent microscopic and X-ray characterization of the solid material collected.

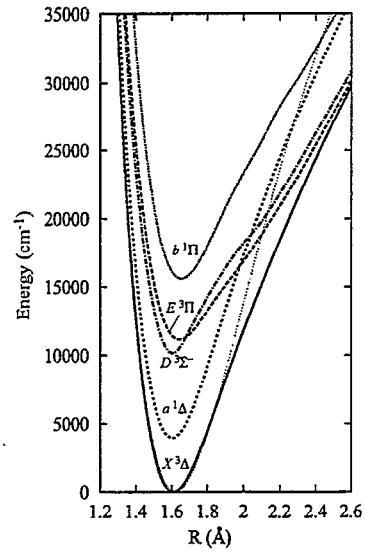


Figure 2. Computed potential curves for the *A*, *E*, *a*, *b* and *D* states of TiO. The lines are cubic spline fits to the SA-CASSCF/IC-MRCI points.

We have completed a study of titanium oxide formed by the reaction of Ti atoms with various oxidant gases. The jet-cooled sample was probed by a beam from a single frequency Ti:sapphire laser in the E-X band system of the radical. The data were fit to an effective Hamiltonian describing the rotational and fine structure levels and parameters describing the structure and electronic properties were determined.

Our understanding of the bonding in the low-lying electronic states of TiO, derived from these and other experimental results, was then compared to computational results obtained using the MOLPRO suite of *ab initio* quantum chemistry programs. SA-CASSCF/IC-MRCI calculations employing both Effective Core Potential (ECP), for titanium and all electron basis sets were performed. Fig. 2 shows computed potential curves for some of the lowest states of TiO. The curves show the large number of low-lying states present, due to the large number of empty or partially filled molecular orbitals of similar energy even in such small species.

Comparison to the experimental curve shows calculations with ECP basis sets that underestimate the stability at longer bond lengths. This is due to the fact that the ECP basis is optimized to the properties of the atom, which is, therefore, computed to have proportionally greater stabilization than the molecule at long r.

The situation is still more complicated in transition metal carbides, which are the primary focus of this program. For these species, experiment is some way behind theory, optical spectra are poorly characterized at best, and we have begun a series of calculations for titanium and molybdenum carbides.

Very little is known about the low-lying electronic states of the TiC molecule. Our calculations at the SA-CASSCF/IC-MRCI level employing an ECP basis for Ti confirm that the ground state is of $^3\Sigma^+$ symmetry, but indicate that the lowest $^1\Sigma^+$ state is only 386 cm^{-1} above it. We have computed the potential energy curves of two $^3\Sigma^+$, two $^3\Pi$ states, two $^1\Sigma^+$ states, and one $^1\Pi$ state as shown in Fig. 3. The corresponding transition dipole moment functions, μ_x and μ_z, are shown in Fig. 4.

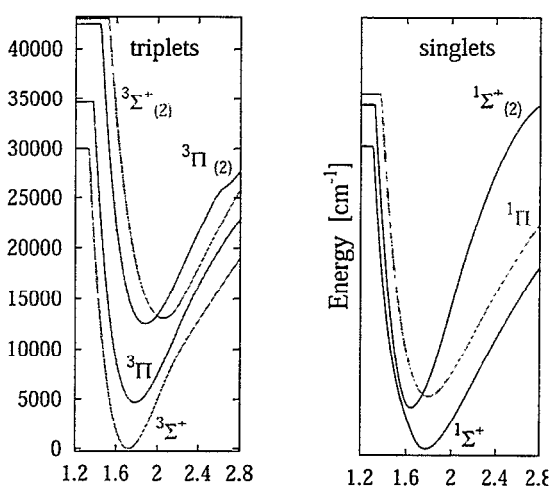


Figure 3. MRCI potential curves based on CASSCF(8 el./10 orb.) reference functions for low-lying singlet and triplet states of TiC.

We have also performed *ab initio* calculations on the TiC_2 molecule, which is believed to be a "building block" in the chemical formation of met-cars such as Ti_8C_{12}. This is a strongly bent molecule with a Ti-C bond length of about 2.1 Å and a C-Ti-C bond angle of about 36°, depending on the electronic state in question. The troubling aspect of these calculations is the level of theory required to obtain an unambiguous ordering of the low-lying electronic states. Only in calculations in which electron correlation is treated at an extremely high level is it clear that the ground state of TiC_2 is a $^3B_1$ state and not the low-lying $^3A_2$ state.

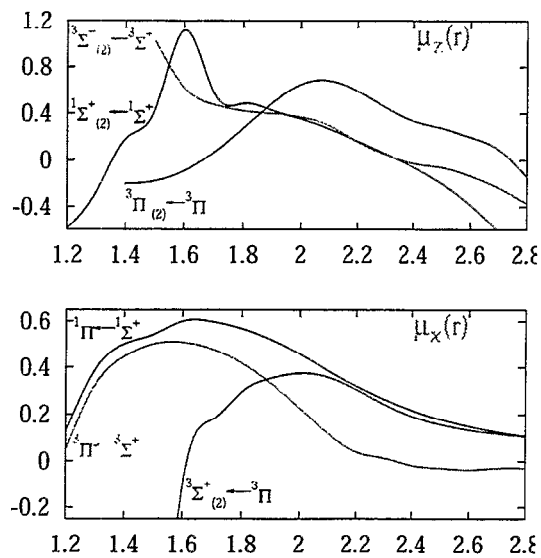


Figure 4. MRCI transition dipole moment components (in Debye) for low-lying $\Pi \leftarrow \Sigma^+$, $\Sigma^+ \leftarrow \Sigma^+$ and $\Pi \leftarrow \Pi$ electronic transitions of TiC.

Finally, we have investigated MoC, which is a species of particular interest in the context of catalysis. We have computed the low-lying electronic states of this molecule at the SA-CASSCF/IC-MRCI level of theory. As shown in Fig. 5, there are very few allowed electronic transitions between states of MoC at this level of theory because of the wide range of spin multiplicities and orbital angular momentum of its valence states. Calculations are under way that include

spin-orbit coupling, which splits many of these states into components with projections of total (electronic plus spin) angular momentum that have more allowed transitions.

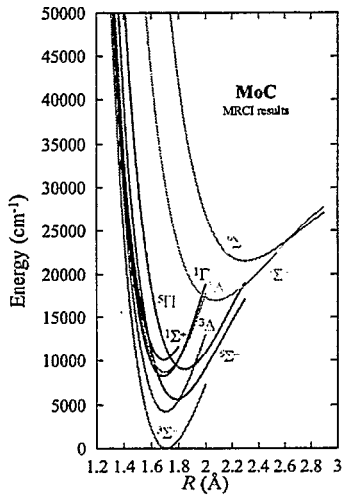


Figure 5. MRCI potential curves based on CASSCF (10 el./10 orb.) reference functions for the eight lowest electronic states of MoC.

The goals for FY2002 in broad terms are to begin an experimental search for spectra of TiC_x and MoC_x using the tools developed during our work on titanium oxide. The experimental work will be guided by the computational results described above. Electronic spectra of TiC will certainly contain the information needed to determine whether the singlet excited state is indeed as low-lying as calculated. We anticipate that the initial searches will be conducted at SUNY Stony Brook, in Professor P. Johnson's laboratory. The LDRD funding is covering a full-time graduate student at Stony Brook working on this project. The experiment at Stony Brook is more suited to the broad spectral searches required in the early stages of the work. At BNL, we intend to make the first spectral measurements incorporating mass-resolved ion detection of metal-containing species in our instrument. This scheme should enhance the sensitivity of the experiment in addition to improving the versatility of the experimental apparatus.

Computationally, the MoC calculations are on going. Already, our results for small molecular fragments imply that extremely high levels of electron correlation need to be included in order to predict correctly the ground state symmetry. With this caveat in mind we have begun calculations of the electronic structure of the met-car Ti_8C_{12} at the Hartree-Fock level of theory. This and larger MoC clusters will form the focus of the theoretical effort in the coming year.

SPECIFIC ACCOMPLISHMENTS:

The $E^3\Pi$ - $X^3\Delta$ transition of jet-cooled TiO observed in absorption, K. Kobayashi, G. E. Hall, J. T. Muckerman, T. J. Sears and A. J. Merer. Journal of Molecular Spectroscopy (in press)

Application of frequency-modulated laser absorption spectroscopy to transition metal containing radicals, K. Kobayashi, G. E. Hall and T. J. Sears. Posters presented at the 16th Annual Symposium on Chemical Physics, University of Waterloo, Waterloo, Ont., Canada, Nov. 3-5th, 2000.

FM Spectroscopy of the TiO E-X transition, K. Kobayashi, G. E. Hall, T. J. Sears and A. J. Merer. Contributed talk at 56th OSU International Symposium on Molecular Spectroscopy, June 11-15, 2001, and Journal of Molecular Spectroscopy (in press)

Calculating rovibronic spectra of transition metal carbides, N. M. Poulin, J. T. Muckerman and T. J. Sears, Poster presented at the XVIIIth Conference on the Dynamics of Molecular Collisions, July 15-20, 2001, Copper Mountain, Colorado.

LDRD FUNDING:

FY 2001	$103,067
FY 2002 (budgeted)	$107,000
FY 2003 (requested)	$107,000

Development of a UV-Raman, Near-field Scanning Optical Microscope for *in-situ* Studies of Chemical Intermediates on Metal Nanoparticles

Michael G. White *01-24*
M. Wu

PURPOSE:

In this project, we propose to establish the feasibility of using UV Raman spectroscopy as a basis for near-field scanning optical microscopy (NSOM) with chemical information. The project involves (1) the demonstration of the high sensitivity of UV resonance-enhanced Raman spectroscopy for detecting chemical species at very low surface concentrations on model nanoparticle systems; (2) feasibility studies for using UV Raman spectroscopy in spectromicroscopy using aperatureless near-field scanning. This project addresses a major goal of nanoscale imaging by providing an approach to index topography with spectroscopic (chemical) information. Such *ultra*spectromicroscopy would find applications to current research on the structure and reactivity of nanoparticles used for catalysis, and in soft-matter research involving bio-macromolecules and polymers.

APPROACH:

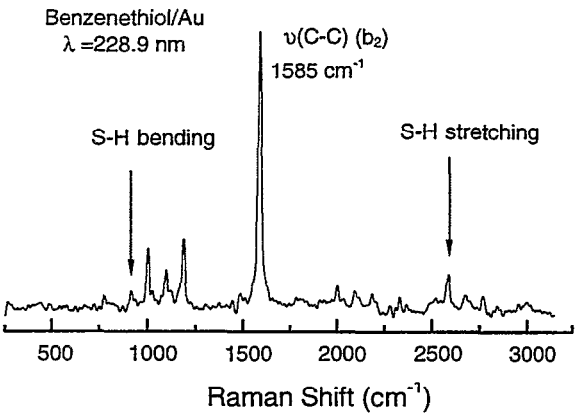
The main issues for spectromicroscopy with NSOM are the conflicting requirements imposed by the use of hollow fiber tips typically used to transmit light to the tip-surface interaction point. On the one-hand, the small exit apertures required for lateral spatial resolution are currently fairly large, 30-50 nm, however, the light transmission of such tapered tips is extremely small, ranging from 10^{-3} to $2x10^{-12}$ as the diameter of the fiber core is reduced from 100nm to 20nm. In addition, the inside of such hollow fiber tips must be coated with a reflective metal (typically Al) to enhance transmission and prevent light leakage outside the tip. Such coatings, however, are easily damaged and thereby place constraints on the input laser power. As a result, NSOM has been limited to light scattering, transmission or fluorescence detection of nanometric features or substrate materials. In this work, we will explore NSOM designs using Raman spectroscopy to obtain chemical information. This choice is based on (1) the general applicability of VIS-UV Raman to a wide variety of chemical environments (vacuum, ambient, liquids); (2) the use of well-known surface enhanced Raman scattering (SERS) and resonance enhancement processes which can significantly improve the surface sensitivity of Raman scattering, particularly for noble metal surfaces or particles (e.g., Al, Cu, Ag, Au); (3) the ability to use UV excitation wavelengths (220 - 260 nm) which provide additional ν^4 Raman scattering enhancements and are better matched to apertureless NSOM designs due to a smaller diffraction limit. In addition, we will explore apertureless designs for near-field scanning, in which the excitation laser is focused onto the tip-sample interaction region and the Raman scattered light is collected by a condensing lens and dispersed by a monochromator for spectral analysis. Spatial contrast results from enhanced Raman scattering in the vicinity of the metallized scanning tip, which is coated with a SERS active metal (Ag, Au,...). Such apertureless NSOM (ANSOM) designs have recently appeared in the literature and have obvious advantage of eliminating the hollow fiber tip and its associated limitations.

Initial work will focus on the sensitivity of UV Raman spectroscopy for detecting molecular adsorbates on metal and metal oxide surfaces at very low coverages. This part will be expanded to include UV Raman investigations of metal-containing nanoparticles or arrays. The second part of this project is to develop an ambient Raman microscope to engineer the basic optical configuration for spectroscopy and assess the sensitivity for small, diffraction-limited spot sizes (~700 nm). Implementation of ANSOM will be performed using a commercial ambient NSOM which is to be modified for apertureless operation. This work will be performed in the UV Raman instrumentation laboratory of M. Wu.

TECHNICAL PROGRESS AND RESULTS:

FY 2001: An ultra high vacuum sample chamber was constructed for UV Raman sensitivity experiments on molecules adsorbed at low coverages on extended surfaces (metal foils, single crystals) and nanoparticle arrays. Studies of pyridine on Ag, benzenethiol on Cu and Au (see Figure), and sulfur dioxide on Ag and TiO_2 (100) surfaces indicate that for molecules with electronic states that can be accessed by the UV excitation (264.3 nm - 228.9 nm), UV Raman provides sufficient sensitivity to detect adsorbates at very low coverages. The UV resonance enhanced spectra also exhibit unusual intensity variations which is a result of mode specific vibronic couplings with the electronically excited state.

FY 2002: Spectroscopy experiments are being expanded to MoS_2 nanoparticle arrays using 2D templating on a Au(111) surface. The latter will be used to assess resonance Raman techniques for investigating the nanoparticle material as well as reactive adsorbates (e.g., thiophene). Optics and



hardware for converting an existing Leica optical microscope into a confocal Raman scanning microscope have been purchased and coupling to a Raman spectrometer is currently underway. The confocal Raman microscope is expected to be completed in FY 2002.

Continued support for this project beyond the LDRD funding period is expected to come via the BNL NanoCenter in which specific requests for laboratory space, instrumentation and manpower support for spectroscopic NSOM development was requested.

SPECIFIC ACCOMPLISHMENTS:

The UV Raman studies of adsorbates at low coverages will be submitted for publication in FY 2002. Data from preliminary Raman studies performed in this project were also used as supporting materials in BNL nanoscience proposals, *Catalysis on the Nanoscale* and *BNL NanoCenter*, submitted to DOE in FY 2001.

LDRD FUNDING:

FY 2001	$ 96,203
FY 2002 (budgeted)	$100,000
FY 2003 (requested)	$100,000

Nanoscience Interests

John Z. Larese *01-26*

PURPOSE:

Use of combined diffraction (neutrons, x-rays), electron microscopy and thermo-dynamic methods to understand and modify the growth characteristics of novel metal oxide particles (Larese/Kunnmann technique) or films, having the general chemical formula $R_xM_{1-x}O$ (where R=Mg, Zn, Cu and M=Ni, Cr, Mg, Zn, Ag, Au, Li). In addition, develop methods to synthesize large quantities of carbon nanotubes for use in studies of adsorption and gas storage. The primary aim is to explore how changes in the composition and morphology of these materials affect the physical, chemical, mechanical, and magnetic properties.

APPROACH:

One avenue to pursue is to use *in-situ* small angle x-ray (or neutron) scattering to "observe" the growth pathology of these materials during synthesis. Our preliminary results indicate that by changing the hydrodynamic (flow) conditions and the crucible orifice design, control of the particle size and morphology is possible. Want to be able to control and modify this process to produce pure and doped materials including "nanowhiskers."

TECHNICAL PROGRESS AND RESULTS:

This project was aimed at developing a capability to examine the production of nanosized metal oxide particles produced via the technique developed by the PI, J. Z. Larese, and W. Kunnmann using neutron and x-ray scattering methods. Some success in producing gold deposits on the MgO particles was achieved as demonstrated by TEM analysis at Washington University. X-ray diffraction analysis also confirmed this finding.

An apparatus to grow the nanotubes was built and tested, and it worked fine. After several months of testing we eventually were able to produce carbon nanotubes of reasonable quality and of reasonable quantity. Metal oxide work was principally focussed on the design of an apparatus for synthesizing metal oxides *in-situ* on the beamline at NSLS. Our efforts were terminated mid 2001 due to a leave of absence taken by the PI.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2001	$28,333

Development of New Techniques for Improvements in PET Imaging of Small Animals and Other Applications

David J. Schlyer *01-28*
C. Woody

PURPOSE:

The ultimate goal of this research is to design and build a detector that employs the latest technology in gamma ray detection to achieve the best possible energy and position resolution for PET imaging. It can then be used for a variety of applications such as freely moving small animal imaging and determination of blood radioactivity non-invasively. We will replace the photomultiplier tubes on standard PET tomographs with avalanche photodiodes (APD), along with their individual readout electronics on each crystal, and compare the images and optimize the parameters of the system. The scope of this LDRD includes the use of this detector to measure blood flow in situ non-invasively. Obtaining an arterial input function will have an immediate impact on our program. This is a very innovative use of these detectors and could prove to be very valuable not only to Brookhaven, but to the entire PET community. It would mean that the use of arterial lines (and the associated risks and pain) could be eliminated from kinetic PET studies. As a next step we will develop the microelectronics necessary for these arrays and use this assembly to image the levels of radioactivity in the blood as it passes through the wrist with high temporal resolution.

APPROACH:

The basic approach to the experiments is outlined below. We are currently in the midst of accomplishing goals one and two of this study.

1. Replace the phototube readout of the present module with avalanche photodiodes (APD) and compare the images. Optimize the image by tuning various parameters in the system, such as APD gain, electronic gain, noise, etc.

2. Achieve a two-dimensional image with the detector array and show that the sensitivity of the array is sufficient to obtain an arterial input function.

3. Replace the traditional electronics with integrated circuits that are compatible with use as a blood monitoring system. If necessary, the crystal arrays can be made larger to increase the sensitivity.

The risk associated with this approach is that the electronics do not exist in the form required to make this type of small ring detector. The development of these electronics would be a great leap forward in PET imaging technology. Other centers are working on such approaches, but no one to date has produced a final product. We feel we have the unique blend of resources to make this happen at Brookhaven.

TECHNICAL PROGRESS AND RESULTS:

The lutetium oxyorthosilicate (LSO) blocks have been assembled with the APD arrays attached. All the electronics associated with reading out the signals from these detector blocks have been assembled and tested. The preliminary results from these tests look very promising and work continues to define the parameters that will be required in the

final application. Specific integrated circuits will be attached to the detector block in order to read out the signals and convert them into an image.

The test set-up has been completed and data is being taken. The acquisition of all the electronics for this project was very time-consuming since 64 separate channels for the data acquisition were needed. We now have this data acquisition system in full operation and have obtained preliminary data. The data acquisition and analysis to determine the exact parameters of the integrated circuits is underway. The design for the wrist detector has been developed and will be tested as the results from the test apparatus are recorded. The final proof of the concept will be the acquisition of a two-dimensional image using the LSO crystals backed by the APD arrays. The sensitivity of this apparatus will determine the size of the array needed in the final device to accurately measure the arterial input function.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2001	$86,322
FY 2002 (budgeted)	$90,000
FY 2003 (requested)	$90,000

Development of CZT Array Technology for Synchrotron Radiation Applications

Peter P. Siddons *01-30*

PURPOSE:

Establishment of the technology to enhance the capabilities of NSLS beamlines by providing advanced detector capabilities. In particular, pixellated detector arrays made from a high-Z material are not currently available, and such devices are essential for designing efficient experiments at x-ray energies greater than 10keV.

APPROACH:

As part of a CRADA project, scientists in the Instrumentation Division (ID) Large Scale Integration (LSI) group have recently developed a Complementary Metal Oxide Semiconductor (CMOS) charge-sensitive preamplifier which is optimized for use with solid-state detectors based on CdxZn1-xTe. BNL has extensive experience in silicon detector technology, both for high energy physics applications and for synchrotron radiation applications. There are many instances for which silicon is ineffective as a detector material for x-rays. In particular, the absorption (and hence detection) efficiency falls very rapidly for photon energies greater than 10 keV. Many non-spectroscopic applications of synchrotron radiation are moving towards higher photon energies as a way to reduce sample absorption artifacts and to provide better bulk probes. Such applications would greatly benefit from the availability of a high-Z detector material and the technology for forming special-purpose arrays from this material. The main problems involved in applying Cadmium Zinc Telluride (CZT) to detectors are the crystal perfection required and the difficulty in making reliable surface electrical contacts to the material. Access to the surface analytical tools available at NSLS should provide valuable scientific input to the contact problem, and diffraction imaging should at least allow us to select high quality areas of a wafer in a non-destructive way, and may provide valuable input to the crystal grower in steering growth technique developments.

P. O'Connor and Z. Li, both from the ID, and S. Hulbert from NSLS are investigators associated with this project. O'Connor's primary input will be in the design of readout circuits for any devices we fabricate. Li is the ID's expert on silicon device fabrication, and we expect to have valuable input from him in this general area. Hulbert is an expert on photoemission and will provide expertise in characterizing device surfaces and interfaces. We have succeeded in attracting a student, but due to visa restrictions, he is not yet expected to arrive until March. The bulk of his support will be provided by his country of origin.

TECHNICAL PROGRESS AND RESULTS:

Progress has focused on establishing the basic infrastructure required for fabricating devices.

We have taken over and refurbished a clean-room facility which was constructed some years ago by IBM. The identification of this facility was essential since the materials we use are incompatible with silicon processes, and hence we were not able to use those facilities available in the ID.

We have procured equipment for semiconductor device fabrication, such as a lithography mask aligner, an electrical microprobe station and associated measurement instruments, and a manual

wire bonder. These are all in house and operational.

We have also procured some raw material for device fabrication. We have chosen to investigate InP, in addition to CZT, as base materials. CZT is better developed as a spectroscopic detector material, but InP has, in principle, some superior electrical properties which make it attractive for high-speed applications.

In FY02, we expect to complete most of the goals outlined in our mid-year report. In particular, we expect to have working single devices or few-element arrays by the end of FY02.

SPECIFIC ACCOMPLISHMENTS:

None.

LDRD FUNDING:

FY 2001	$106,592
FY 2002 (budgeted)	$107,000
FY 2003 (requested)	$106,000

New Applications of Circular Polarized VUV-Light

Elio Vescovo *01-31*
I-G. Baek
S. Hulbert

PURPOSE:

Our goal is to provide the capability to conduct spin- and angular-resolved photoemission experiments with circular polarized light at the U5UA beamline at the NSLS. This beamline is dedicated to the investigation of the magnetic properties of ultrathin films. The use of circularly polarized light will greatly benefit these studies. Particularly, electronic states which cannot be selected with linear light will be available for investigation with circular light. Additionally, circular polarized light allows one to directly resolve spin-orbit split electronic pairs. These electronic states are at the origin of magnetic anisotropy and their study is highly important both for basic understanding of magnetic materials as well as for device applications of the magnetic properties of thin films.

APPROACH:

In recent years, the availability of circularly polarized light (CPL) at synchrotron radiation sources has steadily increased. With the advent of third generation light sources, new insertion devices (e.g. elliptical undulators and wigglers) have provided more intense and brighter CPL than that from out-of-plane bending magnets. Consequently, more demanding experiments, e.g. photoemission and microscopy, have become practically feasible using CPL. However, the energy range usually covered by these new sources is in the soft x-ray region. These high photon energies are not suitable for angle-resolved photoemission (ARPES), an experiment typically performed in the photon energy range 10-100 eV. Recently, it has been suggested that an efficient way to produce CPL at these low energies is to convert linearly polarized light into circularly polarized light using a quadruple-reflection (QR) circular polarizer.

The U5UA undulator beamline - an intense and highly linearly polarized VUV light source in the photon energy range 10-200 eV- is an ideal candidate for a QR polarizer. The addition of a QR circular polarizer is extremely convenient because it tailors the output polarization without any other change to the optical design of the beamline.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001 a QR circular polarizer has been successfully installed and tested at U5UA. This constitutes the only source of circular polarized VUV-light at NSLS. The intense linearly polarized undulator light (LPL) can now be changed to 100% CPL by the QR circular polarizer in 20-50 eV photon energy range. Less pure circularly polarized light can also be obtained up to about 70 eV. Depending from the photon energy the decrease in intensity varies from a factor 10 to a factor 100, in fair agreement with theoretical calculations.

Magnetic circular dichroism and spin-resolved PES spectra of the Fe/W(110) valence band have been collected. They demonstrate that indeed the use of circularly polarized light enhances spectral features which are barely visible with linearly polarized light.

In FY 2002, we plan to continue this project by substituting the U5UA end-station with a new one, presently under construction. This is a critical step because this end-station is

based on a more efficient electron spectrometer. The current analyzer has a radius of 50 mm, the new one of 125 mm. The increase in collection efficiency is expected to compensate the intensity loss due to the QR.

A new postdoctoral appointee, Dr. Hangil Lee (originally from KRISS Institute, South Korea) has been hired and will continue the work of Mr. In-Gyu Baek, particularly focusing on the commissioning of the new photoemission apparatus.

SPECIFIC ACCOMPLISHMENTS:

In-Gyu Baek, Steven Hulbert, and Elio Vescovo, *Performance of a quadruple reflector circular polarizer in VUV region for angle- and spin- resolved photoemission spectroscopy*, Rev. Sci. Instr. 2001 (in press)

(Poster) E. Vescovo, In-Gyu Baek and S. Hulbert, *U5UA Highlights*, Spintronics 2001, Georgetown University, Washington, 9-11 August 2001

(Poster) In-Gyu Baek, Steven Hulbert, and Elio Vescovo, *Quadruple reflector circular polarizer in VUV region for angle- and spin-resolved photoemission spectroscopy*, RSI-Meeting, Madison, Wisconsin, 22-24 August 2001.

LDRD FUNDING:

FY 2001	$23,860
FY 2002 (budgeted)	$45,000
FY 2003 (requested)	$50,000

Soft X-ray Magnetic Speckle

Cecilia Sanchez-Hanke *01-32*
C-C. Kao

PURPOSE:

Develop the necessary experimental technique and computational algorithm for measuring and reconstructing magnetic speckle patterns. The principal application of this work will be imaging magnetic domain structures with sub-micron spatial resolution, and the study of magnetic domain dynamics. Both are important in the understanding of magnetism and the control of magnetic properties on the nanometer scale, a scientific thrust area in the BNL Nanocenter.

APPROACH:

To observe speckle patterns, spatially coherent light is necessary. With increasing brightness from undulators in synchrotron light sources, x-ray speckle patterns have been observed in hard as well as in soft x-ray energy ranges. In the soft x-ray case, there are two major advantages: (1) coherent x-ray flux is proportional to the square of wavelength, (2) large charge and magnetic resonant scattering amplitudes for 3d and 4f elements. Both factors together will make the technique sensitive to very small amounts of magnetic materials, such as self-assembled nano-magnetic particles and nano-patterned magnetic arrays. In addition, the wavelength of interest is on the order of a few nanometers, which means the spatial resolution of this technique will be on the order of tens of nanometers, ideally suited for the study of nanometer-sized magnetic systems.

Experimentally, a 10-micron pinhole will be used at the end of beamline X1B at NSLS to take out coherent soft x-rays. The scattered x-ray, i.e. the speckle pattern, will be recorded using a two-dimensional charge-coupled device (CCD) detector. Speckle patterns will be recorded at selected wavelengths around an absorption edge of the element of interest to provide the phase information necessary for the reconstruction procedure. This is analogous to the multi-wavelength anomalous diffraction (MAD) method routinely used in solving the phase problem in protein crystallography.

Onur. T. Menteş, a graduate student in the Physics Department of the University of Stony Brook, has been recruited to assist in this project.

TECHNICAL PROGRESS AND RESULTS:

On the theoretical side, a reconstruction algorithm has been developed. It is based on the strong magnetic resonances of 3d and 4f elements in the soft x-ray region as described above. The algorithm was tested successfully by reconstructing simulated magnetic speckle patterns generated from an artificially defined magnetic domain pattern.

On the experimental side, speckle patterns from self-assembled Fe nano-particles and Co/Pt multilayers were collected on recent experiments conducted at the X-1B beamline at the NSLS. These data sets are currently being analyzed.

We have also initiated collaboration with the group of Janos Kirz and Chris Jacobsen from the Physics Department of Stony Brook to construct a new experimental chamber. The new chamber will add flexibility and improve the spatial resolution by a factor of two. The design of the chamber is finished.

SPECIFIC ACCOMPLISHMENTS:

"Reconstruction of Magnetization Density in 2-Dimensional Samples from Soft X-ray Speckle Patterns Using Multiple-Wavelength Anomalous Diffraction Method," O. T. Menteş, C. Sánchez-Hanke and C-C. Kao. Submitted to Journal of Synchrotron Radiation.

LDRD FUNDING:

FY 2001	$41,173
FY 2002 (budgeted)	$45,000
FY 2003 (requested)	$50,000

Prototype Approaches Toward Infrared Nanospectroscopy

G. L. Carr *01-35*
L. M. Miller

PURPOSE:

Infrared microspectroscopy with synchrotron radiation is used to locally probe the chemical and electronic properties of materials with a spatial resolution of about 10 μm. But higher spatial resolution (1 μm or better) is needed for studying biological processes within single cells and the physical properties of heterogeneous materials found in environmental, geological, and even space sciences. This project intends to identify and test various methods for increasing the spatial resolution.

APPROACH:

The spatial resolution for conventional (far-field) infrared microspectroscopy is controlled by diffraction. One approach for improving spatial resolution parallels various techniques already in use for visible light microscopy, e.g., optical systems with increased numerical aperture, confocal optical systems, and image deconvolution. The practical limit on spatial resolution using these techniques is not known for infrared microspectroscopy. Though the resolution may never be significantly better than 1 μm, the spectroscopic data from this approach can be interpreted according to standard methods.

The alternative approach is based on near-field techniques where one uses an infrared source having dimensions smaller than a wavelength (and the diffraction limit), and places the sample in close proximity to this source. The technique can be quite inefficient, leading to very poor signal-to-noise. Also, the resulting spectra can be difficult to interpret.

The approach offering the best performance and potential for use with synchrotron radiation is not known. We are actively studying far-field methods to determine the true limits and establish benchmarks for comparison to future near-field methods. We are monitoring near-field techniques and collaborating with other groups (e.g., D. Adams and O. Cherniavsky of Columbia University) to gain understanding in this area.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, the U4IR beamline at the NSLS was modified and an infrared microscope system (formerly at beamline U10B) was installed and aligned. A high-resolution positioning stage was added to this microscope and interfaced to its computer system and software.

A high numerical aperture optical system based on ZnSe hemispherical optics was designed, including a 100 μm diamond surface layer for protection. Optical modeling indicated this layer thickness would not degrade the optical performance (a thin diamond-like coating was not available). Detailed analysis of the point-spread-function for the microscope's Schwarzschild optics was performed and indicated a significant benefit for the confocal arrangement.

Noteworthy accomplishments include:

- Resolution tests for a confocal optical system showed a factor of 3 improvement over a non-confocal system. Studies of a test specimen

indicated a 4 μm resolution at a 7 μm wavelength.

- As a step toward image deconvolution, lateral scans across a sharp edge of photoresist material were performed for detailed comparison with point spread function calculations agreement.
- In addition to sensing lateral (i.e. transverse to the optical axis) variations in material properties, the confocal system was demonstrated to be capable of sensing depth variations (along the optical axis) for some sample geometries.
- A type of near-field microscope system based on a scanning Pt RTD thermometer and AFM was used with synchrotron radiation to produce a spectrum from polystyrene (Columbia University collaboration).

Milestones for FY 2002 include: 1) testing of diamond-faced ZnSe hemispheres on realistic specimens to achieve a spatial resolution of λ/3 or better, 2) testing a type of near-field technique based on scanning thermal microscopy (from Columbia University), and 3) writing software for performing PSF deconvolution for image enhancement.

SPECIFIC ACCOMPLISHMENTS:

Publications and Reports:

1. *Resolution limits for infrared microspectroscopy explored with synchrotron radiation*, G.L. Carr, Rev. Sci. Instrum. 73, 1 (2001). (refereed journal, original manuscript prior to this LDRD, revisions based on LDRD work)
2. *Solid immersion lens for improved spatial resolution in IR microspectroscopy*, M. Ramotowski et al, NSLS 2000 Annual Report (some work prior to this LDRD).
3. *Resolution studies of Schwarzschild-type infrared microscope objectives*, G.L. Carr, NSLS 2001 Annual Report (submitted).
4. *Vertical depth profiling by confocal infrared microspectroscopy*, G.L. Carr, NSLS 2001 Annual Report (submitted).
5. *Scanning Thermal Infrared Microspectroscopy with Synchrotron Radiation,* O. Cherniavsky, D. Adams, and G.L. Carr, NSLS 2001 Annual Report (submitted).

LDRD FUNDING:

FY 2001	$33,689
FY 2002 (budgeted)	$45,000
FY 2003 (requested)	$50,000

Pressure-Induced Protein Folding Monitored by Small-Angle X-Ray Scattering and Fourier Transform Infrared Microspectroscopy

Lisa M. Miller *01-36*
C-C. Kao

PURPOSE:

Develop novel time-resolved methods for studying the structure and dynamics of folding proteins monitored by synchrotron-based, small angle x-ray scattering (SAXS) and Fourier transform infrared micro-spectroscopy (FTIRMS). This project takes advantage of the high brightness of synchrotron radiation, where x-ray and infrared beams can be focused through the small aperture of a flowcell or diamond anvil pressure cell. The NSLS has several beamlines that are well-suited for performing SAXS and FTIRMS, and also has an accomplished user base in designing high-pressure diamond anvil cell devices. These new techniques will become key elements in the ongoing development of the Macro-molecular Structure and Dynamics program at the NSLS.

(http://nslsweb.nsls.bnl.gov/infrared/macromolecules/).

APPROACH:

With over 3 gigabases of DNA in the human genome sequenced, more than 30,000 genes that code for individual proteins have been identified. The Human Proteome Project is the next step in deciphering the human genome and involves identification of the structure and function of each of these proteins. BNL's initiative, The Human Proteome Project, seeks to develop BNL as "a center for producing proteins and determining structures." X-ray crystallography has become the most commonly used technique for determining protein structure and "the NSLS is one of the most efficient of the synchrotrons that is the workhorse of structure production." However, crystal structures provide a "snapshot" of a protein in a single (most often native) state. Thus, it is difficult to learn about protein dynamics (e.g. protein folding and enzymatic function) with an x-ray crystal structure. Also, this technique is difficult to perform on macromolecular complexes and membrane-bound proteins.

This project involves the development of new methods for determining protein structure in solution (instead of the crystallized state) that takes advantage of the unique capabilities of the NSLS.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, a rapid-mix flowcell was designed for determining time-resolved protein structures using Fourier transform infrared micro-spectroscopy. This work was done in collaboration with Dr. Mark Chance (Albert Einstein College of Medicine). Jacyln Tetenbaum, an Energy Research Undergraduate Laboratory Fellowships (ERULF) student, determined the steady-state protein structure of soybean trypsin inhibitor in its native and disulfide-reduced, denatured state using a combination of circular dichroism (CD), x-ray absorption spectroscopy (XAS), and Fourier transform infrared micro-spectroscopy. Dr. Lin Yang (LDRD postdoctoral fellow) has designed and built a SAXS setup on the NSLS insertion device beamline, X21. Software for infrared data analysis was designed and

written in Matlab by Dr. Haluk Utku (LDRD visiting scientist).

For FY 2002, Jim Ablett (LDRD postdoctoral fellow) will determine the structure of native and disulfide-reduced soybean trypsin inhibitor using SAXS. He will also modify the rapid-mix flow cell for CD and SAXS and extend these techniques to additional protein systems. In addition, he will begin the development of a diamond anvil cell for pressure-induced protein folding studies.

SPECIFIC ACCOMPLISHMENTS:

Publications:

FY 2000: N.S. Marinkovic, A.R. Adzic, M. Sullivan, K. Kovac, L.M. Miller, D.L. Rousseau, S.R. Yeh, M.R. Chance (2000). Design and implementation of a rapid-mixer flow cell for time-resolved infrared micro-spectroscopy. *Rev. Sci. Instr.*, **71**: 4057-60.

FY 2001: J. Tetenbaum, L.M. Miller (2001). A new spectroscopic approach to examining the role of disulfide bonds in the structure and unfolding of soybean trypsin inhibitor. *Biochemistry*, **40**: 12215-9.

Abstracts:

FY 2000: L.M. Miller, D. Vairavamurthy, A. Vairavamurthy (2000). Disulfide bond formation in the folding of Ribonuclease A monitored by sulfur x-ray absorption spectroscopy. *Biophys. J.*, **78**: 44A.

FY 2001: J. Tetenbaum, L.M. Miller (2001). When bridges collapse: The role of disulfide bonds in the structure and folding of soybean trypsin inhibitor. *Biophys. J.*, **80**: 563A.

Grant Proposal Pending:

NIH, "In situ analysis of protein structure" 10/01/02 – 09/30/04, $200,000.

LDRD FUNDING:

FY 2001	$43,499
FY 2002 (budgeted)	$45,000
FY 2003 (requested)	$50,000

Soft Condensed Matter Probed by Low-energy Resonant Scattering

Wolfgang A. Caliebe *01-38*
L. Yang

PURPOSE:

The purpose of this LDRD is to apply resonant scattering to the study of soft condensed matter. The resonantly scattering atom is a low Z atom, so that low-energy x-rays between 2 and 3keV have to be used. In resonant scattering, the scattering factor is a tensor, and the intensity of the scattered radiation depends on the dipole moment of the molecule. This allows for the measurement of superstructure reflections which are not observable with conventional x-ray scattering techniques. The intensity and position of these superstructure reflections gives important information about the structure of the sample. The successful implementation of this technique will add another important tool for the investigation and study of soft condensed matter.

APPROACH:

Resonant scattering at conventional x-ray energies of 8keV has proven to be an important tool in the research of magnetic materials, where the orientation of the magnetic moment results in a superstructure of the lattice. An analog in soft condensed matter is, for example, a thin freestanding liquid crystal film in which the dipole moment of the molecule points into different directions in different layers. This superstructure has significant influence on the properties of the liquid crystal film and therefore on its technical application. Conventional methods like x-ray diffraction or laser scattering might just indicate the presence of the superstructure, but the actual periodicity is not accessible. Measuring the superstructure reflections and determining their polarization dependence can solve this problem.

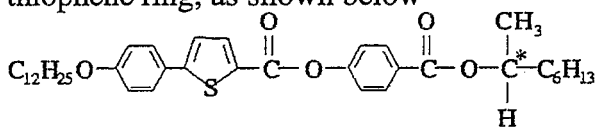
The research on liquid crystal films and similar systems is done in collaboration with Ron Pindak, potential NSLS staff member C.C. Huang and Andrew Cady from the University of Minnesota, where the laser scattering experiments are performed, and Philippe Barois from the University of Bordeaux, France.

The focus of the research at the NSLS is resonant scattering with polarization analysis. The main problem is to overcome the problem of absorption of low-energy x-rays by air, but to keep the sample still in a non-vacuum atmosphere. Most organic thin films are not stable in vacuum. Furthermore, the temperature of the films has to be controllable, and the film itself has to be observed with a normal microscope with polarization filters to determine its integrity and phase transitions. Another important aspect is the development of a polarization analyzer. Most existing polarization analyzers are difficult to align or very heavy. This part is done in collaboration with Peter Siddons, NSLS.

TECHNICAL PROGRESS AND RESULTS:

Three different experimental runs (fall 2000, spring 2001 and fall 2001) permitted the study of several materials and testing of new methods and equipment. In fall 2000, the first version of a newly developed polarization analyzer was tested, and several compounds were studied. The experience of this first experiment resulted in several improvements of the polarization analyzer and the experimental set-up, which were implemented in the following experiments.

The most exciting results were found in the compound MHDDOPTCOB with a thiophene ring, as shown below



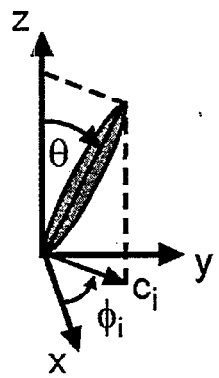


Figure 1: The azimuthal orientation of the liquid crystal molecules in the ith layer is described by the angle Φ_i or by the vector $\mathbf{c}_i$.

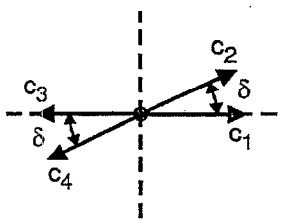


Figure 2: The biaxial model of the repeat unit. The azimuthal orientation of the molecule changes from layer to layer with a 4-layer repeat unit.

In earlier experiments, this compound showed quarter-order satellites. In this experiment, a splitting of the quarter-order satellite was observed with different intensities of both peaks.

As can be seen in Fig. 3 the numerical simulations clearly demonstrate that the biaxial model fits the data very well. Other models could not reproduce the intensity ratio. The results of this experiment were recently published and presented at different conferences.

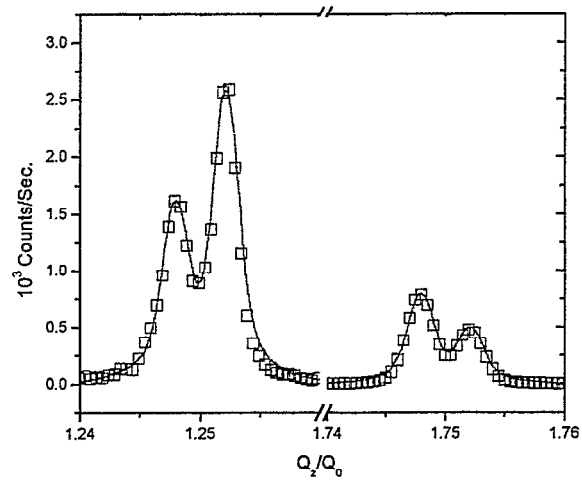


Figure 3: Experimental and theoretical data of resonant diffraction of MHDDOPTCOB in the smectic C^*_{F12}-phase. The calculations use δ=15°.

These experiments proved again that the technique is important for a better understanding of the structure of liquid crystals films and that the hardware developed for these recent experiments works well but can still be improved.

The recent experiments in fall 2001 concentrated on a variety of different samples and methods to study thin films. Spreading the film with two knife-edges is quite time-consuming, and some compounds even do not form freestanding films. Therefore, we tried to make thin films by spreading the compound on a microscope slide and in a small trough. The quality of these films was not as good as that of free-standing films, but they nevertheless still diffracted quite well and also showed superstructure reflections. Compounds studied in this experiment also included banana-shaped compounds with chlorine or sulfur groups. Also the chlorinated compounds showed relatively strong superstructure reflections, although previous experiments with bromated compounds did not show any superstructure reflections.

Further experiments are planned for FY 2002 that will focus more on the banana-shaped compounds. Also, a small kappa-goniometer acquired by the NSLS will be mounted in a large tank which can be evacuated or flushed with helium. This goniometer will be dedicated for research using low-energy x-rays. The existing set-up uses helium-flushed flight paths, which limit the accessible momentum range. The large vacuum tank and its accessories will be funded by the NSLS.

SPECIFIC ACCOMPLISHMENTS:

Invited talks:
P. Barois, "Resonant X-Ray Scattering from Smectic C phases with Antiferroelectric Order and Related Subphases in Bulk Geometry" 6th European Conference on Liquid Crystals

R. Pindak, "Resonant X-Ray Scattering from Antiferroelectric and Ferrielectric Liquid Crystal Films" 6th European Conference on Liquid Crystals

Ron Pindak, APS March meeting 2002

Publications:
Orientational ordering in the chiral smectic-C^*_{F12} liquid crystal phase determined by resonant polarized x-ray diffraction, A. Cady, J. A. Pitney, R. Pindak, L. S. Matkin, S. J. Watson, H. F. Gleeson, P. Cluzeau, P. Barois, A.-M. Levelut, W. Caliebe, J. W. Goodby, M. Hird, and C. C. Huang, Phys. Rev. E 64, 050702(R) (2001)

LDRD FUNDING:

FY 2001	$32,873
FY 2002 (budgeted)	$45,000
FY 2003 (requested)	$50,000

Femto-Seconds Electron Microscope Based on the Photocathode RF Gun

X. Wang *01-39*

PURPOSE:

The objective of this work is to explore the photocathode RF gun technology for femto-second time-resolved electron microscope applications, especially the time-resolved electron diffraction. By taking advantage of higher energy and electron beam energy correlation from the photocathode RF gun, our approach would allow us to break the pico-second time barrier for the first time with an electron microscope. The electron microscope based photocathode RF gun can produce high electron beam energies and shorter electron pulses. Higher energies would make it possible to image bulk material, which is critical for biological applications. Shorter electron pulses will make it possible to study dynamic process. Furthermore, electron beams with bunch lengths on the order of 100 fs are needed to investigate the deterministic process for chemical reactions (comparing to slower, diffuse process). A femto-second electron microscope based on the photocathode RF gun could be used to study atomic rearrangements during the phase transition in condense matter physics, ultra-fast structure transition in biology, and molecular movements during chemical reactions.

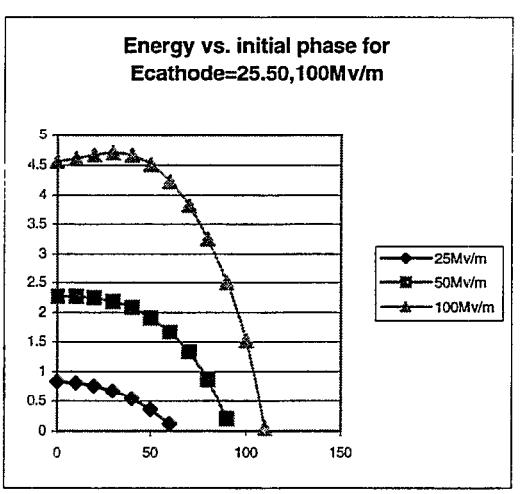
APPROACH:

To make a microscope based on a photocathode to be productive in possible future applications, a stable and reliable complete system will be developed during this project. The complete system consists of sub-picosecond laser, photocathode RF gun as electron source, electron beam imaging system, femto-second electron beam diagnostics and image detector. We will also develop the high power photocathode RF gun laser system so it can also used for pumping for the pump-probe experiment.

TECHNICAL PROGRESS AND RESULTS:

During FY 2001, we have carried out R&D on all major components:

1. Femto-second electron beam dynamics: computer simulation was performed to investigate the electron beam dynamics and the special space charge effect for ultra-short electron beams. We demonstrated the possibility to produce 100 fs (rms) electron beams with a 500 fs laser pulse by ballistic compression. Further electron beam compression is possible using a 30 cm long chicane magnet. We also identified for the first time that it is possible to produce electron beams with extremely small energy spread (< 0.01%) with a photocathode RF gun by operating at near 50MV/m field with sub-picosecond laser (see figure below).



2. Sub-picosecond laser system: we have completed the design of an all solid-state laser system based on a Yb:glass laser oscillator. This laser system not only will be used to drive the photocathode RF gun, but also be used as a pump for pump-probe type experiments. The laser system will be able to produce 10 mJ energy with a rep rate 10 Hz. It will also be synchronized with an RF system with a timing jitter of less than 500 fs.
3. Femto-second electron beam diagnostics: an RF kicker cavity will be used for electron beam bunch length measurements. This technique will be time domain, and capable of self-calibration. With small transverse emittance the time resolution for this technique will be less than 100 fs.
4. Photocathode RF gun: all parts of the photocathode RF gun have been machined; final brazing and assembly will be accomplished in FY 2002.
5. Detector: in collaboration Quantum Electronic Laboratories, Inc, we have carried out tests of a diamond detector at the Accelerator Test Facility (ATF) using x-rays. Initial results are very promising. We would like to test it for electron beam detector use in the future.
6. Electron beam imaging and transport line: a solenoid magnet for electron beam focusing and imaging was built and tested. It satisfies the design requirements.

SPECIFIC ACCOMPLISHMENTS:

X.J. Wang, Progress And Future Directions in High-Brightness Electron Beam Sources, Proceedings, invited talk presented at 2001 Particle Accelerator Conference, Chicago IL. June 18-22, 2001.

X.J. Wang, *et al,* Critical Issues in Photo-injector Performance. Proceedings, 2001 International FEL Conference, Darmstadt Germany, August 20-24, 2001.

X.J. Wang, "Issues in High-brightness Electron Beam Generation", Invited talk presented at Second Asian Particle Accelerator Conference, September 17-21, 2001. Beijing, China.

LDRD FUNDING:

FY 2001	$145,593
FY 2002 (budgeted)	$ 60,000

First-Principles Theory of the Magnetic and Electronic Properties of Nanostructures

Michael Weinert *01-45*
R. E. Watson

PURPOSE:

The goal of this project is to develop a theoretical atomic-scale understanding of the properties of complex materials using state-of-the-art electronic structure calculations, particularly in systems where structural and elemental modulations occur on the order of nanometers. Addressing these questions requires developments in electronic structure theory and the implementation of these advances in computational codes that will of necessity make use of massively parallel computers. The study of nanoscience is a major initiative worldwide, and the research supported here is important to the development of nanoscience and materials science programs at BNL.

APPROACH:

The dimensions of artificial structures that can be fabricated are continually shrinking. Accompanying these advances, there has been a paradigm shift in the physics community from studying ideal uniform systems to studying complex systems. At this length scale, quantum effects play an important role in determining the properties. The interest in nanostructures arises from the possibility that the properties may be influenced by changes in the atomic structure. At present, a fundamental understanding of the properties on the atomic or nano-scale is often lacking. These complications provide the possibilities that theory and/or experiment will uncover new effects, possibly even some with technological applications.

We use first-principles approaches to study the electronic and magnetic properties of complex and nanostructure systems, and then to couple these results to simpler methods that can deal with larger length or time scales. A major interest thrust is understanding the response of systems to externally applied electric and magnetic fields. The calculations are based on density functional theory. A major effort in this project is the development of codes that are capable of treating the large system sizes necessary. G. Schneider at BNL has been essential to this aspect.

The types of scientific problems of interest include interfaces between nanoparticles and host systems, ordering of defects, phase stability and coexistence, and electronic and structural properties of materials. An important aspect of the work is the interaction with experimentalists on properties of "real" materials.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, a significant fraction of time (equivalent to more than 1 FTE) was spent developing the computer codes. The codes are based on the Full-potential Linearized Augmented Plane Wave (FLAPW) method, which is generally acknowledged to be the most accurate approach available. The new features of the codes are the use of completely general symmetry and the extension (via parallelization) to much larger systems sizes. In addition, the codes can include external electric fields self-consistently. The structure and energetics of Mg-Si nanoscale precipitates in aluminum were investigated. Such precipitates occur commonly in alloys and are important to the

mechanical properties, but it is difficult to get atomic scale experimental data since they are metastable. It was found that the Mg-Si impurity interactions are the driving force for the formation, but that Al vacancy-impurity interactions are strong and necessary because they enable diffusion. The interface structure was determined theoretically and shown to have large (~0.1 nm) relaxations. From the calculated interface energies, which vary depending on orientation, it was shown that minimum size particles are needed for stability relative to separated impurities.

The discovery of the new superconductor MgB2 provided an opportunity to make use of the computational developments in collaboration with experimental work at BNL, particularly pressure-dependent x-ray diffraction. The material was found to be surprisingly isotropic (3D) in its elastic properties, although there is (small) change in c/a ratio as a function of pressure. The system does, however, have important 2D character in the B bands, which were compared to photoemission results. In addition, models of other properties of MgB_2 were developed and compared to experiment.

The effect of electric fields on the magnetic properties of Fe(001) surfaces were studied. It was shown that there is a coupling of the electric field to the magnetic moment, including changes in the surface moments.

The distribution of lattice constants in CeO_2 nanoparticles was investigated in order to interpret x-ray studies. The results indicate that the observed changes in lattice constants can be understood simply in terms of Madelung effects.

In FY 2002, the ability to treat step edges and related nano-patterned systems will be included; inclusion of correlation effects within the"LDA+U" approximation, further parallelization, and non-collinear effects will be also be worked on.

SPECIFIC ACCOMPLISHMENTS:

C. McGuinness, K.E. Smith, S.M. Butorin, J.H. Guo, J. Nordgren, T. Vogt, G. Schneider, J. Reilly, J.J. Tu, P.D. Johnson, and D.K. Shuh. *High resolution x-ray emission and absorption study of the valence band electronic structure of MgB_2.* Europhysics Letters **56**, 112 (2001).

M. Rasamny, M. Weinert, G.W. Fernando, and R.E. Watson. *Electronic structure and thermodynamics of defects in $NiAl_3$.* Phys. Rev. B**64**, 144107 (2001).

J.J Tu, G.L. Carr, V. Perebeinos, C.C. Homes, M. Strongin, P.B. Allen, W.N. Kang, E.-M. Choi, H.-J. Kim, and S.L. Lee. *Optical studies of charge dynamics in c-axis oriented superconducting MgB_2 films.* Phys. Rev. Lett. (submitted).

T. Vogt, G. Schneider, J.A. Hriljac, G. Yang, and J.S. Abell. *Compressibility and electronic structure of MgB_2 up to 8 GPa.* Phys. Rev. B**63**, 220505(R) (2001).

Y. Zhu, A.R. Moodenbaugh, G. Schneider, T. Vogt, Q. Li, G. Gu, D.A. Fischer, and J. Tafto. *Unraveling the symmetry of the hole states near the Fermi level in the MgB_2 superconductor.* Phys. Rev. (submitted).

LDRD FUNDING:

FY 2001	$88,387
FY 2002 (budgeted)	$90,000
FY 2003 (requested)	$91,000

Cryo-EM for Solving Membrane Proteins

James F. Hainfeld *01-50*

PURPOSE:

To establish a facility at BNL to examine frozen-hydrated membrane proteins by electron microscopy, and to use this facility to solve unknown structures of important membrane proteins.

Background: Cryo-Electron Microscopy is a preferred method to solve membrane protein structures, since it has been generally unsuccessful to crystallize them in 3-D crystals large enough to be solved by x-ray crystallography (at the NSLS). Because 90 % of drugs target membrane proteins and they are so essential to life, there is intense interest in obtaining their structures. They play a central role in microbial cell remediation, biomass energy, and understanding the cellular machinery. Both NIH and DOE (with its Genomes to Life program) have strong funding initiatives in these areas. This program will pave the way for more intense effort in this area at BNL.

APPROACH:

The scope of this work involves a) instrumentation, b) biochemistry, c) data collection, and d) data reduction. For instrumentation, existing electron microscopes (EMs) on site would be utilized and adapted for cryo work; additionally, cryo-EM facilities at other institutions would be used. Certain other specialized equipment is also necessary, such as a plunge freezer for preparing samples, a cryo transfer system, and a cold stage with regulated temperature and tilting capability. With respect to the biochemistry, membrane protein samples need to be isolated and formed into 2-D crystalline arrays. In order to get enough protein, it may be necessary to develop expression systems. Data collection consists of examining the samples at very low electron dose (to preserve high resolution) and taking many images along with electron diffraction patterns. Finally, the data needs to be processed, correcting for the transfer function of the microscope, and combining data sets and tilts using (typically) Fourier analysis. A 3-dimensional reconstruction is then computed to visualize the protein structure. Work will focus on adapting and using an existing electron microscope, preparation of 2-D membrane protein arrays, and data reduction to obtain 3-D structure maps. These structures will then be interpreted to learn how the proteins function.

Proteins in addition to forming 2-D membrane sheets can also form regular helical structures on lipid tubes or carbon nanotubes. We will therefore investigate this method as well to form membrane protein crystals.

Personnel in addition to P.I.: B. Panessa-Warren was hired on this LDRD as a part-time scientist to operate the electron microscopes, prepare samples, collect EM images and electron diffraction data, develop film, get all the equipment required in place, and prepare carbon nanotubes. M. Becker carried out the obtaining of protein samples and setting up crystallizations. J. Warren assisted in examination of samples by high resolution scanning electron microscopy in the Instrumentation Division and with carbon nanotubes preparation. D.-N. Wang (NYU Medical School) provided the membrane protein: GABA-transporter. B. Gehbrehiwet (Department of Immunology, SUNY-SB) provided samples of the membrane protein: gC1q-receptor. R. MacKinnon (Rockefeller University) provided samples of the membrane protein: K^+ pump. N. Woodbury (Arizona State University) provided samples of the membrane protein: photosynthetic reaction center. R. Glaeser (Lawrence Berkeley National Laboratory) provided samples of the membrane protein:

bacteriorhodopsin. J. Sachs and D. Martin (Department of Medicine, SUNY-SB) provided samples of the membrane protein: Na^+, K^+, ATPase. M. Lewis (Skirball Institute, NYU) assisted in using their cryo-EM facility. S. Wong (BNL and SUNY-SB) assisted with carbon nanotubes.

TECHNICAL PROGRESS AND RESULTS:

2001:

- Two existing transmission electron microscopes at BNL resuscitated
- Cryo tilt stage obtained and tested
- Crystallization of membrane proteins attempted: 1) GABA-transporter, 2) gC1q-receptor, 3) K^+ pump, 4) photosynthetic reaction center, 5) bacteriorhodopsin, 6) Na^+,K^+, ATPase; some produced small crystals
- Crystallization on carbon nanotubes attempted; binding observed but disordered
- Images and electron diffraction data collected; low dose still a challenge
- Plunge freezer partially constructed in shops
- Reconstruction software obtained (Spider and MRC programs) and installed

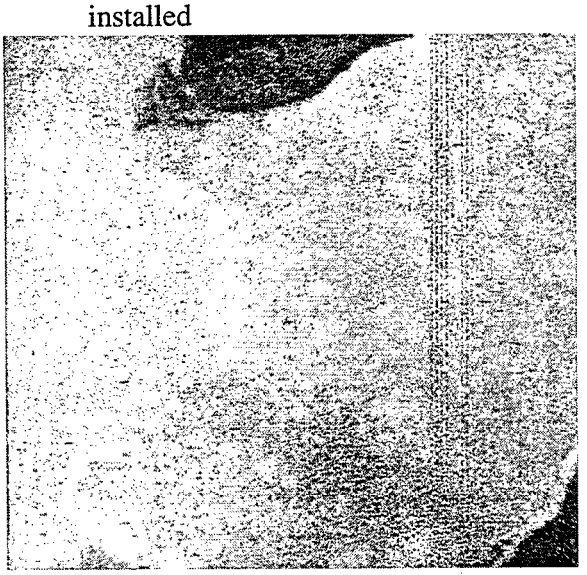


Figure 1: Low dose electron micrograph of hexagonal crystal of the membrane protein bacteriorhodopsin (512 nm full width).

- High performance cryo-EM utilized at NYU

2002 (future work):

- Concentrate on Na^+, K^+, ATPase in different transport states
- Finish construction of plunge freezer
- Obtain high resolution, low dose data
- Utilize new cryoEM that will be delivered in 5 months
- Perform data analysis to solve the membrane protein structure
- Use coulomb-potential map obtained from EM data to compare with electron-density map obtained from X-ray experiments to better understand protein function

SPECIFIC ACCOMPLISHMENTS:

- State-of-the-art cryoEM obtained with DOE funding ($750,000).
- Tenure-track cryoEM position created for new staff member

LDRD FUNDING:

FY 2001	$115,949
FY 2002 (budgeted)	$118,000

Human DNA Damage Responses: DNA-PK and p53

Carl W. Anderson *01-51*

PURPOSE:

Develop and validate methods that will permit a determination of whether mutations and polymorphisms in the non-homologous end-joining (NHEJ) DNA Double-strand breaks (DSBs) repair genes result in increased susceptibility to cancer in humans. This objective will be attained through three specific aims. First, analyze sequences from several human cell lines surrounding the 86 exons of one of the NHEJ DNA repair genes, *PRKDC (gene symbol for the catalytic subunit of the DNA-dependent protein kinase catalytic subunit)*, which encodes the catalytic subunit of the DNA-activated protein kinase, for mutations and polymorphisms. Second, develop a method to inactivate one allele of the PRKDC gene in human cell lines. This methodology would allow one to determine if a mutant or polymorphic allele in cells of a heterozygote containing one normal allele is defective. Third, in collaboration with others, create and analyze endogenous "knock-in" mutations that alter sites of posttranslational modifications in the murine p53 tumor gene. These studies are expected to lead to follow-on funding that enables a full characterization of the consequences of both genetic variation in the NHEJ DNA repair system and its interaction with mechanisms that activate the p53 tumor suppressor system in response to DNA strand breaks.

APPROACH:

To test the hypothesis that polymorphisms in human NHEJ genes may be a risk factor for human cancer, DNA sequences from both normal and cancer populations can be analyzed; however, sequences of the human NHEJ genes, including the sequence of very large catalytic subunit of DNA-PK, were not publically available and therefore had to be obtained. Bacterial artificial chromosome (BAC) clones containing the PRKDC gene and, if required, other NHEJ genes, will be sequenced, and the sequences will be validated by analyzing a small number of cell lines that exhibit normal NHEJ function and one cell line that does not.

To show that a specific polymorphism affects NHEJ function, it will be necessary to examine human cell lines or mice that are homologous for the sequence variation. To accomplish this task, a method to inactivate one or both alleles of the human *PRKDC* gene in established human cell lines will be developed. Deriving such mutant cells currently is technically challenging; for some genes, inactivating mutations may be lethal.

To examine the interaction of NHEJ and p53 as risk factors for cancer, and to develop methods for testing the role of specific polymorphisms in animals, methods will be developed for creating homozygous mutations in specific amino acids of the p53 gene of mice. These studies will be conducted in collaboration with E. Appella, National Cancer Institute, NIH, and Y. Xu, University of California, San Diego. It is anticipated that the methods developed for p53 will translate to the murine *PRKDC* gene.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, the sequence of a 65,000 bp segment of the human gene for DNA-PK$_{cs}$ (*PRKDC*) from a human BAC clone was completed and submitted to the National DNA Databank Genbank (accession number

HSU63630). Analysis revealed several errors in the previously reported sequence of the DNA-PK_{cs} mRNA, including a missing amino acid after residue 2428 in the original cDNA sequence, and an incorrect amino acid in exon 12 most probably resulting from an RT-PCR error during the original cDNA cloning. These errors were corrected in the Genbank reference sequence HSU47077. A frameshift mutation was identified in exon 32 of the *PRKDC* gene from M059J cells, which accounts for the absence of DNA-PK_{cs} in those cells. This result proved that M059J cells cannot make functional DNA-PK. Sequences from 76 and 87 individuals were obtained for exon 12 and exon 32, respectively. Analysis confirmed the identity of amino acid 405 as asparagine rather than tyrosine, and demonstrated that the frameshift mutation from the human glioma-derived M059J cell line is not prevalent in the human population.

The sequence of a 33,000 bp pair region from a BAC clone containing the 3' end of the human PRKDC gene was obtained. Because of the nature of this sequence, several small segments could only be sequenced on one strand of the DNA. Nevertheless, the quality of the sequence in these regions was adequate for submission to Genbank (accession number AY03028). Efforts to complete the double-stranded sequence and to verify the sequence in human cell lines will continue in FY 2002.

Sequence from codon 2140 in exon 48 and codon 3844 in exon 81 were amplified from 96 and 87 humans, respectively. No coding variants were identified in exon 48, and only one individual exhibited a coding variant sequence in exon 81. This variant was at the non-conserved codon 3835 rather than codon 3834 as was observed in the murine *PRKDC* gene. This result demonstrated that polymorphisms in these two exons are unlikely to be a significant cause of breast cancer susceptibility in humans, but did not rule out a role for polymorphisms or mutations in other exons in human cancer.

During FY 2002, efforts will continue to complete sequences around remaining PRKDC exons that have not been identified including exons 39-41, and 49-69. Primers to amplify segments containing these exons and exons 70-86 will be designed, and sequences from four cell lines will be obtained and analyzed. Analysis of the *PRKDC* gene from 12 human breast cancer patients will begin, six of which exhibit a phenotype of chromosomal breakage in response to ionizing radiation. These DNAs were obtained from a much larger collection of breast cancer patients that are part of the Carolina Breast Cancer Study. Because BNL will obtain only coded DNAs and cell lines, an exemption from human subjects requirements was granted. Efforts will begin to develop knockout human cells lines lacking functional *PRKDC* genes.

SPECIFIC ACCOMPLISHMENTS:

Anderson, C. W., J. J. Dunn, P. Freimuth, A. M. Galloway, and M. J. Allalunis-Turner. Frameshift mutation in *PRKDC*, the gene for DNA-PK_{cs}, in the human, DNA repair-defective, glioma-derived cell line M059J. Radiation Research **156**, 2-9 (2001).

NIH R01 CA89199-01, P.I.: Carl W. Anderson, Title: Genetic Variation in Human NHEJ DNA Repair Genes, Project Period: 07/01/01 - 06/30/06, Recommended 5 year total funding: $1,746,916.

LDRD FUNDING:

FY 2001	$167,158
FY 2002 (budgeted)	$168,000

Molecular Mechanisms Underlying Structural Changes in the Adult Brain: A Genetic Analyses

John J. Dunn *01-52A*

PURPOSE:

One goal of this project is to develop methods for Serial Analysis of Gene Expression (SAGE) which use only small quantities of starting material, such as those obtained from brain punch biopsies. Another goal is increasing the length of the sequence tags to provide absolute identification of transcripts.

APPROACH:

For many years our group has been involved in developing technologies based on the genetic elements of bacteriophage T7 in general and T7 RNA polymerase in particular. T7 RNA polymerase provides a means for unbiased amplification of low-abundance RNA samples, such as those obtained from brain punch biopsies. In collaboration with W. Bahou at SUNY-SB, we are studying the ability of T7 RNA polymerase to linearly amplify small amounts of RNA. Our preliminary results indicate that one round of amplification yields a 10^3-fold high-fidelity increase in that amount of starting mRNA and two rounds yields about a 10^5-fold increase. While this work was in progress, we also developed our Long SAGE protocol and verified the methodology by producing and sample sequencing a Long SAGE test library derived from a human erythroid leukemia cell line.

TECHNICAL PROGRESS AND RESULTS:

Two basic principles underlie the SAGE methodology: (i) a short sequence tag from a defined position contains sufficient information to uniquely identify an mRNA and (ii) the linking together of tags in a serial fashion allows for an increased efficiency in sequence-based analysis.

During FY 2001, a modified version of SAGE, called Long SAGE, was developed which generates 21-base long tags rather than the 14-bp long tags that are obtained following the published protocol. This advancement in SAGE technology greatly reduces the ambiguities associated with linking tags to expressed sequences since the probability of encountering a tag sequence at random decreases from once every 4^{14} or 2.68×10^8 bases for 14-base long tags to 4^{21} or 4.39×10^{12} bases when the tags are generated using the Long SAGE protocol. The uniqueness of these 21 bp tags allows them to be directly aligned to the draft human sequence with a high level of specificity. The correspondence of tag position relative to known and *ab initio*-predicted genes in draft sequences allows for direct validation of gene predictions, as well as identification of expressed regions that might have been overlooked without experimental data. This dramatic increase in tag length suggested to us that a Long SAGE DNA-based approach should allow for simultaneous detection, as well as quantification, of all the genomes present in a microbial assemblage. Furthermore, this direct profiling of DNA in microbial communities would sample both cultivatable and currently uncultivatable organisms and at the same time provide the sequence for probes that could be used to identify cloned segments of novel genomes in appropriate

libraries. We have termed the method SAST (for Serial Analysis of Signature Tags) to reflect its retention of the serial aspect of the original SAGE method which lends itself to high-throughput analysis. SAST is viewed as an innovative, high-risk project and it is currently undergoing evaluation at BNL.

As mentioned above, a major breakthrough in SAGE technology was achieved which generates 21-base long tags. This increase in tag length necessitated rewriting our SAGE analysis computer algorithms. We then expanded our analysis to include in silico SAST analysis of 21-base long tags derived from completely sequenced bacterial genomes listed in The Institute of Genetic Research's (TIGR) database. These computer simulations revealed that 21-base long SAST tags can distinguish closely related bacterial species from one another. This ability to interrogate the DNA of related strains and obtain a direct read out of the sequence tags has potential utility in our efforts to detect and respond to biological terrorism.

Long SAGE and SAST tags are important new methods to profile gene expression and genomic diversity. We are collaborating with several laboratories to verify the SAST technology and are attempting to obtain DOE support for using SAST for surveillance and identification of potential biological warfare agents.

During FY 2002, the Long SAGE portion of the project will require access to rodent biopsy samples.

We anticipate that these samples will be processed to generate libraries that will then be sequenced to obtain expression profiles from stimulated and unstimulated brains.

SPECIFIC ACCOMPLISHMENTS:

A patent disclosure covering the emerging SAST technology has been filed with BNL's Office of Intellectual Property & Industrial Partnerships. Both Long SAGE and SAST were presented as enabling technologies at a meeting with funding managers at DOE Headquarters on November 6, 2001. This was followed by a presentation on November 9, 2001, to the BSA Science and Technology Steering Committee as part of a new initiative to develop a Center for the Molecular Analysis of Microbial Communities (CMAMC) within the Biology Department.

We are currently preparing SAST libraries from two closely related bacterial pathogens, *Yersinia pestis* and *Y. pseudotuberculous*, to test the feasibility of whole genomic SAST profiling to distinguish between closely related pathogenic bacteria.

LDRD FUNDING:

FY 2001	$117,218
FY 2002 (budgeted)	$117,000

Catalytic Microcombustion Systems

C.R. Krishna *01-58A*

PURPOSE:

Portable power generation systems of much higher energy densities than batteries are being sought to power computers, communication equipment, etc. by the military and also by commercial manufacturers for obvious reasons. This effectively requires, at least at the present juncture, using a petroleum liquid fuel and a miniature fuel cell or heat engine to convert the chemical energy to electric power. The goal of the project is to lead towards the development of a liquid fueled microcombustion system which is at the heart of a miniature heat engine, more specifically a heat engine that uses a thermoconversion module, similar to thermophotovoltaics (TPV), operating at ambient pressures and at potentially lower temperatures than TPV. The objective is to provide a solution to the problems inherent in all components of such a combustion system, including fuel and air metering, injection and mixing, ignition, stable combustion in small combustion volumes, and emissions from potentially excessive heat losses. The nature of the problems is both fundamental in scope in some of the processes and systemic to the whole. A successful completion could result in the development of new programs, for example with DARPA, and complement the thermophotovoltaic initiative in the BNL institutional plan.

APPROACH:

We have previously investigated different types of fuel injection systems for different fuels. Also, atomization techniques for small fuel flow rates have been pursued culminating in an air atomizer being adapted for the TPV system by Dr. Thomas A. Butcher, who will be a collaborator on the project. The current project requires the development of an injection system, which will operate at an even lower flow rate and which also has a lower parasitic loss. A variety of injection schemes will be considered for the microcombustor before one or more will be tested.

TECHNICAL PROGRESS AND RESULTS:

High-pressure atomization is not feasible for the flow rates envisaged at thermal outputs of 100 watts or so, as the flow determining orifices become very small causing difficulties of fabrication tolerances and clogging in operation. Air atomization, especially using low-pressure air is possible, but the parasitic losses were calculated to be significant. It seemed that a capillary pump would be feasible, as it uses the surface forces between the material and the fuel and hence no energy is required during the fuel injection process. The Washburn model for the capillary flow was used to design the capillary requirements.

A zero dimensional spreadsheet model was developed to generate the overall parameters for the first design of the combustor. Preliminary flame heights were calculated using the Roper version of the Burke-Schumann flame model. This was complemented by axi-symmetric CFD calculations carried out by Dr. Thomas Butcher. A tentative design for a combustor with a capillary pump injection and a regenerative air entry system to preheat the combustion air has been proposed.

During this year, DARPA came out with a request for proposals to develop portable power generation systems that would require microcombustors of the scale and type being investigated in this project. Three organizations with different thermoelectric conversion schemes joined in generating three proposals to DARPA. One of them was partially successful in obtaining funding for a preliminary phase that does not include the combustor. It is anticipated that at least one design will be chosen, constructed and tested. It will be instrumented to obtain basic combustion data to feed into design calculations.

Depending on the extent of success in the combustion tests, we will attempt to add a thermoelectric module purchased from one of the parties that collaborated in writing a DARPA proposal. If the results are encouraging, funding to continue the work will be sought from the army (which has expressed interest in the development of such systems) and/or DARPA.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2001	$93,108
FY 2002 (budgeted)	$96,000

Power Quality and Reliability in Interconnected Microgrids

Thomas Butcher *01-59A*

PURPOSE:

Distributed power generation involves small-scale electricity generation technologies [such as solar photovoltaics, fuel cells, thermophotovoltaics, and microturbines] that are located in close proximity to the loads they serve. These technologies offer the potential for very large increases in the overall efficiency with which energy is used when waste heat from electric power production may be directly utilized [cogeneration]. Such technologies are expected to play an increasingly important role in the future national electric system. Integrating and interfacing this generation from distributed energy technologies with the conventional electric transmission and distribution grid poses many challenges related to system reliability, power quality, and power economics.

This study was planned to develop and apply a set of methods for evaluating the performance, power quality and reliability of distributed generation sources, and establish these BNL methods as standards for the industry. The work is the first study of its kind and was planned to establish BNL and this methodology as the standard approach for assessing distributed generation technologies. The project has contributed directly to the establishment of BNL in the field testing of DG technologies.

APPROACH:

This LDRD Project applies a foundation of technical strengths resident at BNL to perform an innovative analysis of power quality and reliability challenges facing the rapidly growing DG area. This foundation specifically includes: methodologies developed at BNL for the analysis of reliability in nuclear power systems, experience with power quality studies, the existence of fuel cell and microturbine test units, and the BNL program in thermophotovoltaic power generation.

On a power grid "quality" typically refers to the frequency and severity of deviations in the electric supply from a steady, 60Hz, perfectly sinusoidal waveform of voltage or current. The power quality demands of equipment vary considerably, but power quality requirements have generally increased with increased use of computers and other electronic equipment. The cost of poor power quality is very difficult to estimate and includes loss of productivity from equipment downtime. It has been estimated that the cost of poor power quality to U.S. businesses is $15 to $30 billion per year.

Many probabilistic models, methodologies, and tools have been developed within the nuclear power industry over the last few decades that have found wide application in a wide variety of other industries including the aerospace, chemical, power, transportation, medical, and information technology. Methods such as systems analysis, failure modes and effects analysis, fault tree and event tree analyses, reliability block diagrams, goal oriented methods, common cause failures, etc. have been extensively developed and used to predict performance, reliability, and risk associated with undesirable events or outcomes. The ensemble of these models and methodologies is generally known as the probabilistic risk assessment (PRA) methodology. These methods have been applied to the modeling and analysis of systems of varying levels of complexity to identify and assess operational and

regulatory decisions, and the impact of the performance of different technological, human, and organizational elements within these systems.

This work, as planned, involved two major components: power quality analysis and reliability assessment. Michael Villaran and Jerome LaMontagne collaborated with Tom Butcher on the project.

The Energy Resources Division (ERD) conducts research in all aspects of the energy conversion process, including combustion research and improvements in the efficiency of oil-fired furnaces. It has participated in a commercial fuel cell power demonstration project with a manufacturer and the local utility. The recent heightened interest in distributed generation resources, led ERD to pursue work with another fuel cell manufacturer and KeySpan Energy Delivery to construct, operate, and monitor a distributed generation microgrid at BNL.

The main apparatus consists of two Capstone Model 330 MicroTurbines (one natural gas-fired and one fuel oil-fired), capable of generating 30 kW electric each, located outside of Building 526 and one Avista Labs proton exchange membrane (PEM) fuel cell, with an output capacity of 3 kW electric, located inside the building. The power produced by these distributed generation sources will be fed back to the local microgrid through the appropriate electrical connections. One microturbine will be fired by natural gas from the existing natural gas supply at the northeast corner of Building 526. The second microturbine will be fired by fuel oil via an upgraded supply system from the existing fuel oil storage and supply system. An exhaust heat recovery unit will be fitted to the natural gas-fired microturbine to produce heated water for the building hot water system. The Avista Labs fuel cell will be operated by hydrogen gas supplied from a hydrogen manifold and supply system outside of the building. Various operating and output parameters of the microgrid equipment will be monitored and analyzed, and the operation, maintenance, and reliability of the overall system will be tracked.

TECHNICAL PROGRESS AND RESULTS:

A technical literature review was conducted to identify previous research, technical standards, techniques, and parameters involved in monitoring electric power quality and reliability, and more specifically, for distributed electric generation. Power quality monitoring instrumentation and software were selected. A Research, Development, and Demonstration agreement was negotiated with KeySpan Energy Delivery to operate the 30 kW gas-fired microturbine and exhaust heat recovery heat exchanger for one year as part of a demonstration program at which time BNL would obtain ownership of the unit for $1. A 30 kW fuel oil-fired microturbine generator and a 3 kW fuel cell were purchased and delivered to BNL under separate DOE funding.

A general specification for the microgrid at Building 526 was prepared, and Plant Engineering designed and began installation of the plant improvements required to install, monitor, and operate the distributed generation sources. Installation work is ongoing, with completion projected for early in FY2002. The required safety analyses and documentation for the project were prepared and approved by the safety review committee.

This project was terminated after the first year, but some of the planned work is expected to continue with funding from other sources. After the distributed

generation sources have been installed and tested, the microturbines will be operated and monitored as part of a microgrid feeding electric power into the BNL grid through the Building 526 distribution system and heated water into the building's hot water system. The fuel cell will be operated and monitored as it supplies power to dedicated electrical loads.

SPECIFIC ACCOMPLISHMENTS:

The project has been helpful in obtaining the funding for the creation of the microgrid and in obtaining support for the field testing and demonstration of a large fuel cell [250 kW FuelCell Energy] at the Central Utility Plant. In cooperation with BNL Plant Engineering, Federal Energy Management Plan (FEMP) funding has been obtained to integrate one microturbine with the Building 526 heating system for continuous operation in the future.

LDRD FUNDING:

FY 2001	$72,412

Mapping Electron Densities in Porphyrin Radical Crystals Using the NSLS

Kathleen M. Barkigia *01-62*

PURPOSE:

Porphyrins are tetrapyrrole derivatives that mediate a spectrum of bioenergetic reactions ranging from solar photosynthetic energy transduction to conversion of carbon dioxide into fuel. Porphyrin cation radicals, i.e. oxidized porphyins in which an electron is removed from the macrocycle rather than the metal, are important intermediates in the catalytic cycles of heme proteins and in photosynthetic processes. The objective of this work is twofold, namely to assess the stereochemical consequences of oxidation in porphyrin radicals at high resolution and high precision and to determine actual orbital occupancies of the metals and electron populations of the atoms that comprise the porphyrin skeleton. For paramagnetic metals, it can provide insight into the nature of the coupling between the unpaired electron on the porphyrin and those in the metal d orbitals, that is the basis for ferromagnetic or antiferromagnetic behavior. There are no electron density studies on radicals of any type in the literature.

APPROACH:

As part of the Porphyrin Chemistry Program (headed by Jack Fajer), we have designed a variety of biomimetic porphyrin radicals to address the consequences of oxidation in vivo, and have characterized them by multidisciplinary crystallographic, spectroscopic and theoretical techniques. Building on the methods for determining crystal structures from microcrystals at the NSLS that we have already implemented, we have broadened our scope to include extremely high resolution data collection at beamline X3A1 at 20K. The research is conducted in collaboration with Mark Renner (Materials Science Dept., BNL) who prepares the crystals, Philip Coppens, an expert in charge density analysis (SUNY Buffalo) and Guang Wu, the beamline scientist at beamline X3A1. Use of the NSLS has several fundamental advantages over conventional X-ray techniques for intrinsically unstable porphyrin radicals that do not readily form large single crystals. Among them are: 1) a highly intense X-ray beam eliminating the need for big crystals, 2) fast data collection on area detectors at 20K impeding crystal decomposition and enabling high data redundancy, 3) short wavelength (0.643Å) for maximizing resolution.

TECHNICAL PROGRESS AND RESULTS:

Data for several porphyrin radicals and neutral precursors have been obtained. In some cases, multiple datasets were collected. For the radicals, they represent the highest resolution X-ray data ever measured. Typical resolution for porphyrin radical datasets is on the order of 0.75Å; some of these data extend as far as 0.45Å. The compounds[1] studied are:

1. $ZnOEP^{\cdot+}ClO_4^-$ B-B dimer

ZnOEP is readily oxidized to a B-cation radical that can be isolated as a dimer of the aquated perchlorate salt, H_2O-$ZnOEP^{\cdot+}ClO_4$, in which the perchlorate is hydrogen-bonded to the water ligand. The dimer exhibits tight B-B contacts of 3.26Å and an unusual short and long bond length alternation of the inner 16-member ring. This bond alternation is observed at 298K and at 20K (H. Song, R.D. Orosz, C.A. Reed, and W.R. Scheidt, Inorg. Chem., 29, 4274 (1990). In the latter, the differences between long and short bonds

are large and highly significant, at the level of 20 estimated standard deviations.

2. CoOETPP and two different CoOETPP B-cation radicals with ClO_4^- counterions

Because of its distorted conformation, CoOETPP undergoes facile oxidation to stable B-cation radicals. At 20K, the neutral parent assumes an almost pure saddle conformation with large out-of-plane displacements of the core porphyrin atoms. Two of its radicals have also been characterized at 20K. These are monomeric $Co(II)OETPP^{\cdot+}$ ClO_4^-, in which the Co(II) ion is ligated by the ClO_4^- anion and a water-bridged dimer H_2O-$Co(II)OETPP^{\cdot+}ClO_4^-$, linked by hydrogen bonds between the axial water molecules and the ClO_4^- counterions. The radicals show additional conformational distortions compared to neutral Co(II)OETPP. In solution, the radicals are diamagnetic, i.e., the unpaired electron in the d_z^2 orbital of the Co(II) is antiferromagnetically coupled to the unpaired electron on the porphyrin radical.

3. $(dmf)(H_2O)Fe(III)OETPP^{\cdot2+}(ClO_4^-)_2$.

The dication radical is obtained by oxidation of $Fe(III)OETPP^{\cdot+}$. The Fe-N distances are typical of high spin Fe(III). The counterions flank the (H_2O) ligand and are hydrogen bonded to it. Estimated standard deviations on the Fe-N and Fe-O distances are 0.001Å and on typical C-C bonds are 0.002Å, respectively.

4. $Fe(II)(NO_2)_8TDCPP(i\text{-}PrOH)_2$

Introduction of electron-withdrawing chloride substituents on the peripheral phenyl rings and nitro (NO_2) groups directly on the porphyrin framework results in a series of compounds with unusually positive redox potentials. For the Fe(II) derivatives, changing the oxygenous axial ligand modulates the spin state of the Fe(II) center. When crystallized from mixtures of alcohols, such as i-PrOH, the high spin state of Fe(II) is stabilized, as evidenced by the elongated Fe-N bond distances obtained at 20K.

5. Expected milestones in FY 2002.

At this point, we have preliminary results from the population analysis of the valence electrons for the core atoms of two porphyrin radicals. From the conventional refinements of the data where the atoms are treated spherically, we see residuals in the chemical bonds that are indicative of bonding electrons as shown in Figure 1. Based on these promising results, we expect that the subsequent aspherical refinements will provide the occupancies of the d orbitals and the electronic ground states of the metal. In addition, we plan to pursue the study of chlorin (hydroporphyrin) cation radicals and some anion radicals based on the easily reducible $(NO_2)_8TDCPP$ family.

[1]Abbreviations used are: OEP (octaethylporphyrin); OETPP (octaethyltetraphenylporphyrin); TDCPP (tetra-2,6-dichlorophenylporphyrin); DMF (dimethylformamide); i-PrOH (isopropanol).

SPECIFIC ACCOMPLISHMENTS:

Some of these results were presented at the Twenty-fourth DOE Solar Photochemistry Research Conference, sponsored by the Office of Basic Energy Sciences, Tahoe City, CA, June 3-7, 2001.

LDRD FUNDING:

FY 2001	$ 29,102
FY 2002 (budgeted)	$ 70,000
FY 2003 (requested)	$102,000

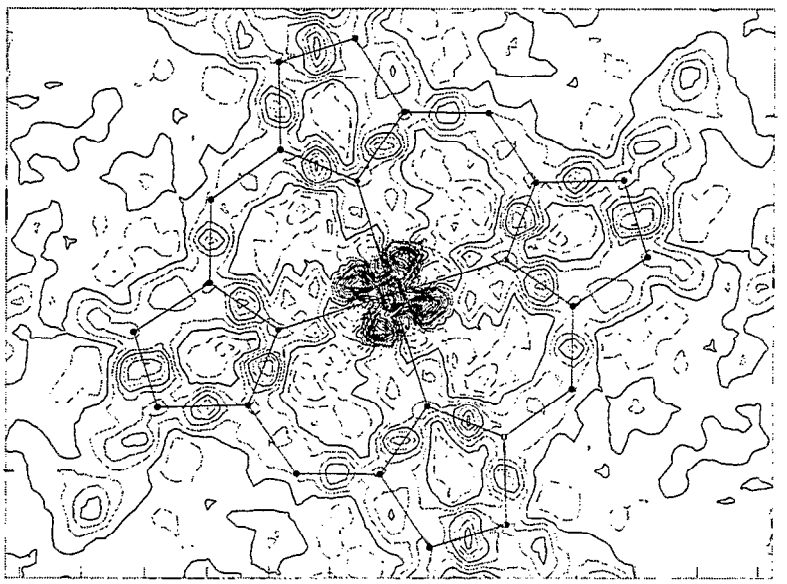


Figure 1. Residual electron density in the plane of the porphyrin after conventional refinement for one of the neutral precursors. Each contour represents 0.10 electrons. Negative density is shown by broken contours.

High Sensitivity Mass Spectrometer

Peter E. Vanier *01-67*
J. Warren
L. Forman, SUNY Stony Brook

PURPOSE:

The purpose of the project is to increase significantly the sensitivity of sector-type mass spectrometers by using multiple ion beams in a pattern established by coded-aperture theory. There are two areas of interest in this development. The first application is for a sensitive hand-held "sniffer," capable of identifying chemical agents and biological weapons related materials for counter-terror applications. This sniffer mass spectrometer uses high-performance rare-earth permanent magnetic materials allowing it to be the first high-sensitivity hand-held system ever built. It is expected to be an important tool in field identification of terrorist production facilities and for field identification of hazards in response to attack. The second application is for use in very high-resolution mass spectrometry used in molecular biology research. In this application, the device should greatly reduce the time required for identification of very massive molecules and contribute to the productivity of the field.

There are requirements for rapid analysis of airborne vapors in environmental monitoring, law enforcement, military scenarios, and in counter-terrorism. At present, the competing technologies that may be used to accomplish rapid analysis are mobile laboratories in vans, or half-tracked vehicles equipped with analytical grade instruments. The availability of a briefcase-sized unit would be very attractive. However, the analytical capabilities will be less than those of a mobile laboratory.

The risk of this project is that the final performance capabilities established by our research, e.g. for a hand-held sniffer, does not prove to be acceptable for the most important uses. For example, the resolution of a small magnetic mass spectrometer using multiple beams requires that the multiple trajectories are not significantly different from theory, including fringing field effects at the entrance and exit pole faces of the magnet. In principle, effects of this type are minimal in large magnets but may be a problem for a small magnet design of a few centimeters radius of curvature resulting in degraded resolution.

APPROACH:

The high-sensitivity source project is an outgrowth of the application of coded apertures to neutron imaging. Coded apertures can increase the data collection rates by combining the beam currents created by multiple slits into a complex pattern that can be deconvolved by algorithms complementary to those that generated the mask pattern. This approach has been most successful for a point source such as in x-ray astronomy from satellites, because the complex image detected is deconvolved resulting in all data appearing in a single pixel. In our application, multiple line source beams are generated with a much higher total output current than a single beam required *for the same resolution.* When scanning the ion beam, the coded aperture pattern from the source aligns with the pattern at the detector only when the mass is correct.

Another area in which BNL expertise is important is in the fabrication of the coded aperture mask. The precise fabrication of the slit arrays for the spectrometer source and exit is essential to producing a mathematically decodable pattern. Modern micro-technology techniques make this possible by photolithography and directional etching.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, measurements made were to verify that the ion beam exiting the output slit of the source was reasonably uniform. This was necessary because the mathematical treatment of the pattern matching assumes all beams from the source have an intensity proportional to beam width. These measurements were carried out using a commercially available electron bombardment source manufactured by Vacuum Instruments, Inc., Ronkonkoma, NY. The results successfully demonstrated that the coded aperture approach could be used.

The second phase of the work was to design and begin construction of the prototype mass spectrometer. Design work is complete on the beam optics and most of the hardware for the mass spectrometer. We have received the vacuum pumping equipment from Varian. The permanent magnet lenses are soon to be delivered.

The first source and detector coded apertures were completed by the Instrumentation Division in October. The slits were defined by photolithography on a (110) face of a silicon wafer, with the slit edges defined by (111) planes. Anisotropic wet etching in KOH at 70°C cuts perpendicular to the wafer at a much more rapid rate than in the direction perpendicular to the slit edges. The high magnification photographs of the collection slit array is shown in Figure 1. This clearly demonstrates the precision in construction of the assemblies made from a silicon wafer of 125-micron thickness.

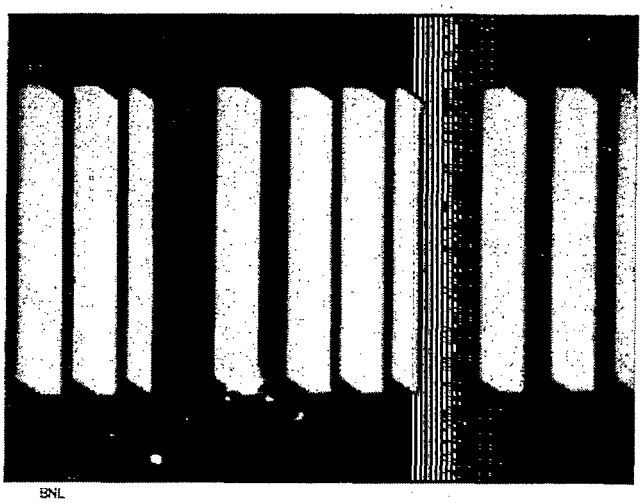


Figure 1. Optical micrograph of coded exit slits etched in silicon wafer

In FY 2002, we shall complete construction of the prototype instrument, test the coded aperture concept, and begin to develop an initial database for chemical vapors of interest to prospective sponsors. We would then be in a stronger position to approach prospective sponsors for funding.

SPECIFIC ACCOMPLISHMENTS:

Proposals have been submitted for funding to two DOE offices involved with counter-terrorism, DOE/NN20 and DOE/IN22; however, the DOE funding in this area awaits coordination with the new Department of Homeland Defense which is first focussing on short-term goals to meet immediate needs.

LDRD FUNDING:

FY 2001	$117,574
FY 2002 (budgeted)	$121,000

Development and Application of Cavity Ringdown Spectroscopy to the Detection and Monitoring of Trace Chemical Species in the Atmosphere

A. J. Sedlacek *01-78*

PURPOSE:

The purpose of this LDRD project is to develop a fieldable instrument based on the technique of cavity ringdown spectroscopy for the ultra-high sensitivity optical detection of trace atmospheric species. The proposed work will focus on the detection of ambient mercury vapor (parts-per-trillion levels) and will examine the efficacy of this approach towards the real-time detection and monitoring of ambient ammonia.

APPROACH:

Over the past decade a new technique known as cavity ringdown (CRD) spectroscopy has provided practitioners of absorption spectroscopy a tool to realize parts-per-billion (ppb) to parts-per-trillion (ppt) detection sensitivities without complex modulation techniques. CRD spectroscopy has been able to achieve this level of sensitivity because this approach measures the *rate of absorption* rather than directly monitoring the change in the probe light intensity. By measuring the rate of absorption, the CRD measurement process becomes independent of light source intensity fluctuations thereby increasing attainable detection sensitivities.

In CRD, a monochromatic light pulse is injected into a high Q-value optical cavity. A detector is positioned at the exit end of the cavity to monitor the light leakage of the injected light pulse per round trip. Using very highly reflective mirrors, the injected laser pulse will make several thousand round trips between the two cavity mirrors. Each round trip will result in a slight loss of intensity due to transmission loses at each mirror and other finite losses in the system. This loss will follow a simple exponential decay. When an absorbing sample is then placed in the cavity, the loss per round trip will exceed that of the empty cavity thereby resulting in a different decay. When this measurement is conducted as a function of wavelength a high sensitivity absorption spectra can be reconstructed for a given chemical species. The time necessary for the intensity (amplitude) of the injected light pulse to decay to 1/e of its initial value is referred to as the "ringdown" time, and from which this spectroscopy derives its name. Typically, the decay time to the 1/e value is on the order of tens of microseconds. Consequently, a CRD signal is collected for each laser pulse and subsequently averaged until the desired signal-to-noise ratio (SNR) is achieved.

TECHNICAL PROGRESS AND RESULTS:

During FY 2001, efforts focused on the construction of a deep-ultraviolet cavity ringdown system which included the refurbishing of a tunable Spectra-Physics MOPO-730 laser system, procurement of ultra-high reflectivity mirrors at 253.6 nm, development of instrumentation control drivers, and initial calibration of the system. The CRD mirrors were fabricated by Los Gatos Research and have a reflectivity approaching 99.8% at the requisite wavelength. These mirrors, which have a radius of curvature of 6 m, are the most critical part of the entire CRD system as the mirror reflectivity dictates the dynamic range or the CRD detection. For example, this level of reflectivity translates to a

ringdown time for an *empty* cell of just ~800 nsec. The addition of mercury into this cell will cause the ringdown time to decrease further thereby requiring a very fast data acquisition system. To address this need a 0.5 giga-sample/sec data acquisition system (LeCroy 9530 DSO) is being used to collect and digitize the ringdown signals. Raw signals are detected using a solar-blind Hamamatsu photomultiplier tube (R1647). Instrumentation drivers were written through an ongoing collaboration with Hofstra University. Finally, a significant effort was undertaken during this first year to refurbish the laser system. This all solid-state, completely tunable laser system (Spectra-Physics MOPO-730) will serve as the laser source for the "on" and "off" resonance wavelengths. With the completion of the deep-UV CRD system, subsystem testing and calibration was undertaken.

In addition to the deep-UV CRD system, the PI has also examined the efficacy of this technique towards the *open-path*, real-time detection of ambient ammonia. Ammonia's basic nature and high water solubility make it a significant player in atmospheric chemistry. Of particular interest is the reaction between ammonia and nitric acid to form an ammonium nitrate particulate.

$$NH_3\,(gas) + HNO_3\,(gas) \rightarrow NH_4NO_3$$

It is because of this role in fine particulate formation that there is a strong desire to resolve ammonia's spatial and temporal behavior with field measurements. Since ammonia is highly reactive, classic "sample-and grab" techniques tend to be complicated because the trapped ammonia can undergo losses due to reaction with the walls of the sampling container prior to chemical analysis. In contrast, an examination of mid-IR CRD reveals that an open-path CRD system would enable the detection of ammonia with a time resolution of 10s at the part-per-trillion loading levels in the atmosphere. This very ultra-high sensitivity can be achieved because of the large absorption cross-section of ammonia in the mid-IR, along with the availability of very highly reflective mirrors that can approach 0.99995.

Future LDRD work in FY 2002 will expand upon the initial subsystem calibration by analyzing air samples for Hg collected as part of a NYC harbor sludge sediments program. The investigator will seek opportunities to collect samples from other laboratories within the DOE complex (e.g., ORNL). It is expected that this exploratory work will lead to the development of a fieldable instrument capable of real-time detection of mercury and ammonia.

ACCOMPLISHMENTS:

Have been in contact with Dr. W. Aljoe from the DOE/National Energy Technology Laboratory (NETLD) on real-time Hg monitoring requirements for the coal combustion community. A proposal is presently being written for the fall solicitation from DOE/Environmental Management (EM).

LDRD FUNDING:

FY 2001	$ 88,000
FY 2002 (budgeted)	$ 88,000

Development of A High Field Magnet for Neutrino Factory Storage Rings

Ramesh Gupta *01-79*
B. Parker

PURPOSE:

Develop and demonstrate a dipole magnet design that can be utilized for a compact Neutrino Factory Storage Ring. Since the storage ring must be tilted, a compact design would minimize the environmental impact as the entire ring can remain above the ground water table at BNL with the top of the ring residing under a modest sized artificial hill. In addition, the magnet is being designed to minimize the energy deposition on the superconducting coils due to showers initiated by muon decay products.

APPROACH:

We are developing a new racetrack coil magnet design with an open midplane gap that keeps decay particles in a neutrino factory muon storage ring from directly hitting superconducting coils. This eliminates the need for an expensive "tungsten liner." These flat racetrack coils have a large bend radius in the ends that allow the use of "react and wind" magnet technology using Nb_3Sn superconductor.

TECHNICAL PROGRESS AND RESULTS:

After exploring several options, we have chosen and optimized the basic magnetic and mechanical design. The cross-section of this design is shown in Fig. 1. The superconducting collared coils inside a cryostat clear the magnet midplane region where most of the decay energy goes. A warm iron yoke structure around the coils then allows heat generated by decay particles to be removed efficiently at a higher temperature.

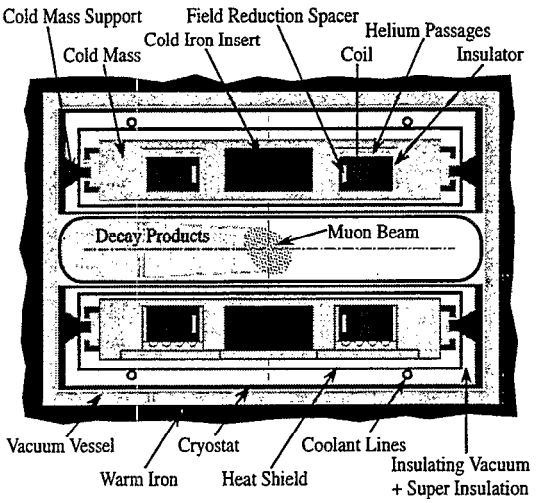


Figure 1: Cross section, with main features labeled, of neutrino factory muon storage ring magnet that avoids decay particles directly hitting superconducting coils.

The dipole operating field is 6.93 T and the design quench field is over 8 T for an operating field margin of over 15%. The maximum field on the conductor at quench is significantly higher than the central field and excludes using NbTi at 4.2 K. The coils, therefore, are made from a brittle Nb_3Sn superconductor. A large bend radius in the ends and a simple pancake coil (racetrack) geometry allows the use of "react and wind" magnet technology.

The superconducting coils are contained in cold masses surrounded by a heat shield and cryostat. Large vertical forces, that could be either attractive or repulsive depending on the configuration, are contained with the help of support keys mounted to the

yoke. The overall magnet structure is designed to minimize the heat leak through the support keys while containing the large Lorentz forces. Finite element analysis codes were used to minimize the deflections and stresses on the superconducting coils and on the support structure.

To maintain field strength, we minimize the vertical distance between the coils and the beam cavity. The cryostat wall thickness is minimized on the side near the beam tube. The beam tube is warm and its thickness is as small as possible. Surrounding both cold masses and the beam cavity is an outer vacuum vessel that eliminates differential pressure on the cryostats and beam tubes and prevents them from collapsing under vacuum. It was observed that a skew quadrupole lattice avoids the direct hit of a large number of decay particles on quadrupole magnets as well. In addition, a novel magnet system design has been developed where all focusing is provided in the ends (see Fig. 2 and Fig. 3).

In Fig. 2 (Design A), the coil packages are longitudinally staggered to provide focusing (F) or defocusing (D) skew quadrupole combined function magnets where there is only a single coil on the top or the bottom. A pure dipole field occurs in overlap regions. The dipole guide field in non-overlap regions is about half that in overlap regions. Thus, the structure has continuous bending and alternate gradient skew focusing. Space normally lost at coil ends and magnet interconnects is efficiently used.

In design B, we propose a novel approach of using small coils with reverse polarity. In addition to making a skew quadrupole, these reverse coils provide an automatic cancellation of normal and skew harmonics in the end region as shown in figure 3. The magnet cross-section has been designed to produce a dipole field with a field error of only about one part in 10,000. This, however, still leaves an axial component of the field in the lattice.

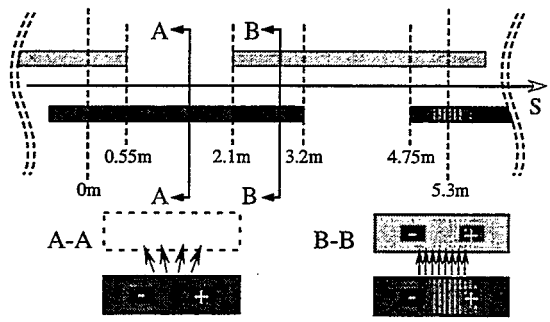


Figure 2: Design-A coil and cryostat layout schematic. Regions with no coil overlap, A-A, have half strength dipole field + skew quadrupole field. Full dipole field and no skew quadrupole occurs in overlap region, B-B.

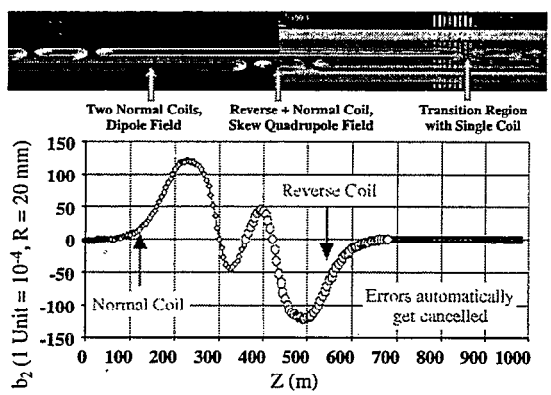


Figure 3: Design-B coil layout and an example of end harmonic cancellation. Since normal and reverse coils have same ends, their coil end field harmonics cancel.

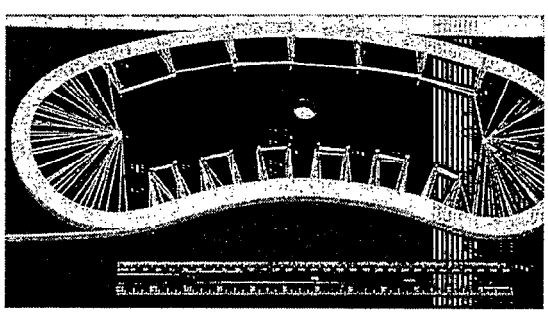


Figure 4: Winding technique for coils with reverse bends.

The coils for compact Neutrino Factory Storage Ring would have a considerable saggitta. Conventional coil construction techniques are not suitable for making coils with brittle material having a reverse curvature. A novel coil winding technique is being developed where the conductor is held in place with Kevlar strings. A successful test run of this concept is shown in figure 4. These curved coils will be vacuum impregnated. To this end we are adopting a "Vacuum Bag" technology for the first time in accelerator magnets.

In FY 2002, we plan to complete the detailed engineering design of the magnet coils. In addition, we also plan to build and test the superconducting coils.

SPECIFIC ACCOMPLISHMENTS:

B. Parker, Skew-Quadrupole Focusing Lattices and Their Applications, 2001 Particle Accelerator Conference, Chicago, 18-22 June, 2001.

B. Parker, M. Anerella, A. Ghosh, R. Gupta, M. Harrison, J. Schmalzle, J. Sondericker, and E. Willen, Magnets for a Muon Storage Ring, 2001 Particle Accelerator Conference, Chicago, 18-22 June, 2001.

S. Ozaki, R. Palmer, M. Zisman, and J. Gallardo ed., Feasibility Study-II of a Muon-Based Neutrino Source, BNL-52623 (2001).

N. Mokhov, C. J. Johnstone, B. Parker, Beam-Induced Energy Deposition in Muon Storage Rings, 2001 Particle Accelerator Conference, Chicago, 18-22 June, 2001.

In addition, several talks were given by principle investigators at various meetings. These include Muon Collider Collaboration Meetings, Editorial Meetings on Neutrino Factory Feasibility Study, Symposium on Neutrino Factory Study II and presentations at Snowmass 2001.

LDRD FUNDING:

FY 2001	$98,066
FY 2002 (budgeted)	$100,000
FY 2003 (requested)	$125,000

DNA-Nano Wires that AutoConnect in 3 Dimensions

James F. Hainfeld *01-82*

PURPOSE:

To investigate the use of DNA strands coated with small gold clusters or further metalized as novel and extremely small nanowires that may be connected at their ends to target junctions by base-pairing hybridization. This could produce wires 150 times smaller than those currently used to make computer chips, permit 3-dimensional wiring, and potentially increase the power of computers by 3,000,000 times.

APPROACH:

We have previously coupled nanometer-sized gold clusters to antibodies and other proteins to visualize molecular sites using the scanning transmission electron microscope (STEM). It appeared that such gold clusters could also be attached to single strands of DNA in high enough density to permit tunneling conduction. Furthermore, we have shown that adjacent gold clusters can be coalesced chemically with additional metal, and this could be used to form continuous metal nanowires. Aspects of this work are to: a) achieve high-density attachment of gold clusters to DNA by various means, b) measure their conductivity, c) further deposit additional metal to form continuous metal nanowires, d) demonstrate hybridization of DNA-metal nanowires, e) study programmed assembly of electronic nanostructures by DNA scaffolding. Methods to carry out this work include: a) chemical synthesis of appropriate gold clusters, b) biochemical techniques to handle and purify DNA constructs, c) use of STEM to visualize products, d) e-beam lithography to produce small electrodes for measuring conductivity, e) optimization of catalytic metal deposition to produce continuous metal nanowires.

Personnel in addition to P.I: J. Warren (Instrumentation Division): produced e-beam lithographic jigs for conductivity measurements. P. Micca (Medical Department): assisted in labeling DNA. R.A. Kiehl (Department of Electrical and Computer Engineering, University of Minnesota): Collaborator working on self-assembled DNA nanostructures that are gold labeled.

TECHNICAL PROGRESS AND RESULTS:

Accomplished in FY 2001:

- Double-stranded DNA labeled to high density using 1.4 nm gold nanoparticles
- Single-stranded DNA labeled to medium density using gold nanoparticles
- oligomers of 26 bases of DNA labeled to high density with gold
- base-pairing hybridization of gold labeled DNA oligomers demonstrated
- purification of DNA-gold structures from excess gold was worked out
- STEM microscopy used to assess results
- self-assembled DNA nanostructures were gold labeled and studied
- demonstrated, for the first time, the assembly of nanoparticle arrays by DNA scaffolding.
- e-beam lithography was used to produce tiny electrodes to measure DNA conductivity

Expected in FY 2002:

- synthesize and use a gold-intercalator construct to tightly and completely coat DNA

- catalytically deposit additional metal to form contiguous metal nanowires
- construct electronics and improved electrodes to measure conductivity of single DNA nanowires
- hybridize ends of a DNA nanowire (form connections) to specific morphologic target points
- explore the use of DNA as a programmable scaffolding for assembling hybrid bioinorganic structures containing arrays of metallic nanoparticles

SPECIFIC ACCOMPLISHMENTS:

- Hainfeld, J.F.; F.R. Furuya; R.D. Powell; and W. Liu. (2001). DNA Nanowires. Proceedings, Microscopy and Microanlysis, 1034-1035.
- Shoujun Xiao, Furong Liu, Abbey E. Rosen, James F. Hainfeld, Nadrian C. Seeman, Karin Musier-Forsyth, and Richard A. Kiehl. (2001) Assembly of Nanoparticle Arrays by DNA Scaffolding. Submitted to Nature.
- Part of this work was submitted to the DOE Nanotechnology Initiative in the BNL proposal, "Charge Injection and Transport in Nanoscale Materials." Limited funding received from this multi-departmental effort was applied only to the Chemistry Department.

LDRD FUNDING:

FY 2001	$58,814
FY 2002 (budgeted)	$60,000

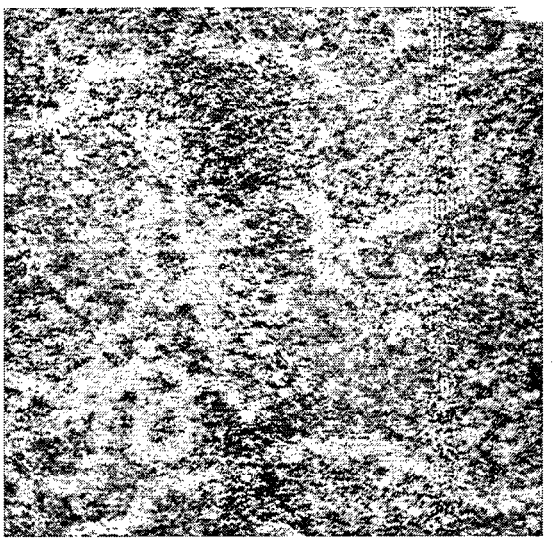


Figure 1. Double-stranded DNA labeled with 1.4 nm gold nanoclusters. Full width 128 nm

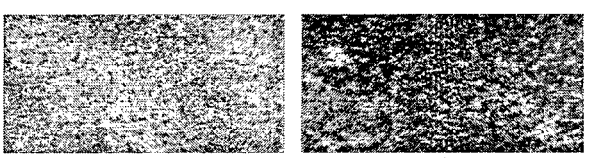


Figure 2. Left: 26-mer oligonucleotide with 1.4 nm gold clusters attached: note either 1,2, or 3 golds are bound to the oligo. Full width of image, 180nm. Right: Two complementary 26-mer oligos were gold labeled, then hybridized and purified. Full width 90 nm (twice magnification of left image).

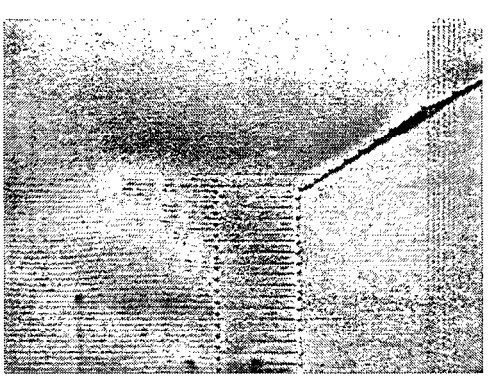


Figure 3. Electron beam lithographic array for measuring DNA conductivity. Array lines are 100 nm in width.

Carbon Nanotube Chemical Probes For Biological Membrane Attachment Quantification

Barbara Panessa-Warren *01-85*

PURPOSE:

Explore the use of "*functionalized*" carbon nanotubes as specific, sensitized biological membrane probes in living cell systems. Carbon nanotube and nanotube-structures (nanoropes, nano-onions or bucky-onions, nano-rafts, etc.) were to be cleaned (when bought commercially) or synthesized and reacted with specific macromolecules for use as membrane probes and to study the dynamic visco-elastic and physical properties of living bacterial spore attachments to surfaces and human cells. By using "*functionalized*" nanotube probes attached to Atomic Force Microscope (AFM) cantilevers, living endospores attached to surfaces such as mica, human cells, glass or agar, can be studied at high resolution. The nature of the attachment of viable bacterial endospores to biofilms (especially thermophile bacteria isolated from Yellowstone National Park hotsprings) and to human cells, is being studied to analyze the initial formation of bacterial-biofilms and the morphology and physical characteristics of bacterial endospore attachments. In light of the recent anthrax endospore terrorism, this research has already been providing immediate data on the mechanisms of spore attachment and human cell colonization/invasion by spores utilizing these new methods in nanotechnology through the BNL initiative in nanotechnology.

APPROACH:

The present methodologies for studying bacterial attachment are labor intensive (marker immuno-labeling by high resolution Transmission Electron Microscope (TEM) and cryo-TEM, fluorescence light microscopy etc.) taking weeks to process specimens for TEM and requiring a large enough specimen to produce adequate signal over the background noise to do fluorescence microscopy. Bacterial **Endospores**, which begin the infectious process for many diseases (i.e. anthrax, pseudomembranous enterocolitis, tetanus, botulism, gas gangrene), as well as start the process of biofilm formation in industry and infection, are too small (0.2-0.5um) for routine fluorescence microscopy even when confocal microscopy is used. TEM requires that specimens are chemically killed and infiltrated with plastic for sectioning or frozen and thin sectioned for analysis. The latter methods allow imaging but do not provide information about the viable, non-chemically-treated membrane response that facilitates the first stage of bacterial attack in spore-forming bacteria. By using the proposed functionalized carbon nanotubes, experiments on attachment and the characteristics of that attachment can be done on living systems which is unique and reveals information not yet possible using any other method. By using the nanotube probes, both dynamic living experiments using AFM and light microscopy can be done as well as glutaraldehyde fixed TEM and Scanning Electron Microscope (SEM) preparations made for comparison. By using functionalized nanotubes on AFM cantilever tips, endospores attached to a substrate or host cell surface can be made to attach to the cantilever tip, and visco-elastic measurements of spore attachment can be made for the first time.

A. Collaborator: Dr. Stanislaus Wong has experience in covalently functionalizing nanotubes for chemistry and biological uses, and he has used these functionalized nanotubes to study adhesion (streptavidin to biotin). He has helped to develop methodologies to clean the nanotubes prior to chemical functionalization, and his skill in AFM has provided the screening of the functionalized tubes prior to biological interaction. Now that his AFM has been installed, calibrated, and is in routine use, the new phase of this project to study the visco-elastic characteristics of spore attachment will be carried out during this coming year.

B. Collaborator: Professor George Tortora, Head, Clinical Microbiology Dept., SUNY Stony Brook, has provided the microbial clinical expertise to isolate the bacterial thermophiles and mesophiles used to test the nanotubes. He provides the microbial expertise and quality control (insuring that cultures are not contaminated) for each of the nanotube-cell and nanotube-bacterial invasion experiments. Dr. Tortora will provide the microbial cultures and his expertise in the interpretation of the biofilm and bacterial aspects of the attachment/invasion.

C. Collaborator: Professor Berhane Ghebrehiwet, Dept. of Immunology, School of Medicine, SUNY Stony Brook, prepares the monoclonal antibodies and receptor proteins for nanotube functionalization and participates in the interpretation of the data.

TECHNICAL PROGRESS AND RESULTS FY2001:

Isolation and Cleaning of Single-Walled Nanotubes(SWNT): Commercially purchased nanotubes were cleaned using several methodologies (to remove inherent graphite and metallic debris [Ni,Co,Fe]). Acid, alkali, detergent, centrifugation, and filtering methods were used to clean nanotubes but produced low yields, and residual debris could not be removed. We were able to make clean nanotube structures (nano-caterpillars and bucky-onions) by developing our own protocols, that were sufficiently clean to react SWNTs with biological antibody and receptor proteins via the use of EDC (1-ethyl-3(3-dimethylaminopropyl) for uptake with cells. Dr. John Warren (Instrumentation Div.) developed the technology to produce our own cleaner, multiwalled nanotubes (MWNT), and a methodology was developed to react labeling proteins successfully to the MWNT (Figure 1).

Using Bacterial endospores to Clean Nanotube Preps: In an attempt to remove graphite and metal contamination, nanotube preparations were reacted with bacterial endospores and the spores with attached nanoropes removed. This method of removing debris from nanotubes was not continued because the spores then aggregated into a tangle of SWNTs resistant to sonication and chemical disaggregation.

Obtaining and Characterizing Cell lines for Project: After canvassing commercial sources nationally, 2 tissue culture cell lines grown as monolayers on coverslips (Diagnostic Hybrids, Athens, Ohio) were found and characterized having the required characteristics (cell growth, consistency, ability to grow in aerobically and anaerobically, surface membrane receptivity and similarity to in vivo human cells).

Reacting Functionalized Nanotubes with Cells: The anaerobic and aerobic incubators were purchased and set-up which allowed the testing of the functionalized nanotubes with the tissue culture cell monolayers. The

cells functioned normally in the presence of the nanotubes (functionalized and plain nanotubes)-no toxic or abnormal growth or behavior. When an antibody to block the invasion protein (for *Listeria* and C.*difficile* invasion) was linked to 3 different types of nanotube preparations, incubated with colon cells, and subsequently inoculated with 5 ul of 0.5 McFarland Listeria bacterial cells or C.*difficile* endospores, the: **1.** carbon nanotube probes formed clusters of aggregations on the colon cell surface ("capping"), and in those areas of functionalized nanotube attachment, the *Listeria* bacteria could not enter the cells (Figure 2). It was possible to see the distribution of the antibody reaction on the cell surface by light microscopy, revealing for the first time where on a living colon cell the gClq-receptors were localized and how this distribution changed with bacterial attack; **2.** Nanotubes functionalized with the gClq-receptor protein were not able to block entry of bacteria, nor were they bound to cell surfaces; **3.** Functionalized nanotubes with anti-gClq-receptor antibody blocked the entry of C.*difficile* endospores into colon cells indicating that bacterial entry may not be genus specific, but may be facilitated by the gClq membrane receptor.

Developing Bacillus Aerobic Species for AFM Attachment Experiments: Two isolates of the thermophiles and meosphiles from Yellowstone National Park hotsprings were sporulated and purified by Dr. Tortora and characterized here at BNL (Figure 3) to provide two species of non-pathogenic test organisms for attachment experiments that produce biofilms and will attach rapidly after heat-shock in air. Dr. Tortora also prepared purified B.*cereus* endospores as a non-hotspring aerobic species for nanotube attachment studies. This *B.cereus* strain is genetically very similar to *Bacillus anthracis* with the exception of making the latter's toxins; and, therefore, the attachment data collected here relates directly to the current anthrax situation without the risk of a Level 3(CDC) organism.

RESULTS AND MILESTONES PLANNED IN FY2002:

1. By using functionalized nanotubes, identify the distribution, frequency and localization per cell of the receptor protein (gClq-r) for *Listeria* and C.*difficile* attachment on colon cells.

2. Identify by TEM whether the nanotubes enter the tissue culture cells or produce any type of independent cellular response (phagocytosis, inflammation, cell death, etc.) that could alter results.

3. Examine by high resolution TEM how the antibody and receptor proteins are: **a.** attached to the nanotubes; **b.**which reactive sites are available for the membrane probe reaction; and **c.** which end of the biological protein is bound to the nanotube.

4. Protein-nanotube attachment: **a.** are the chemicals EDC [1-(3-dimethylaminopropyl) -3-ethylcarbodimide hydrochloride] or benylamine the best linking agents for attachment of bio-active proteins to nanotubes, with the least toxicity to the tissue culture cells and bacterial cells. **b.** Does crystallization of the antibody or receptor protein on nanotubes offer a better approach than chemical EDC-protein linking.

5. Develop quantitative methods for mapping and counting nanotube probes per cell using the low-dose field emission SEM and newly installed archiving system; and see if this can be extended to light microscopy quantification with some accuracy.

6. Visco-Elastic Measurement of bacterial endospore attachments to ligands, bio-membrane receptors and hold-fast surfaces.

SPECIFIC ACCOMPLISHMENTS:

1. Paper presented May 7, 2001, at "SCANNING 2001," Roosevelt Hotel, NYC. "Geothermal and Pathogenic Clostridial & Bacillus Endospore Ultrastructural Attachment Mechanisms," B. Panessa-Warren, G. Tortora, and J. Warren.

2. Preparation of an abstract to the American Society for Microbiology to be submitted November 29, 2001; "Bacillus and Clostridial Endospores Initiate Infective Process," to be presented May 2002.

3. Manuscript to be submitted in November 2001 to NATURE, "Clostridial and Bacillus Endospores Attachment Begins Infective Process." B. Panessa-Warren, G.Tortora, and J. Warren

LDRD FUNDING:

FY 2001	$48,378
FY 2002 (budgeted)	$49,800
FY 2003 (requested)	$48,100

FIGURES

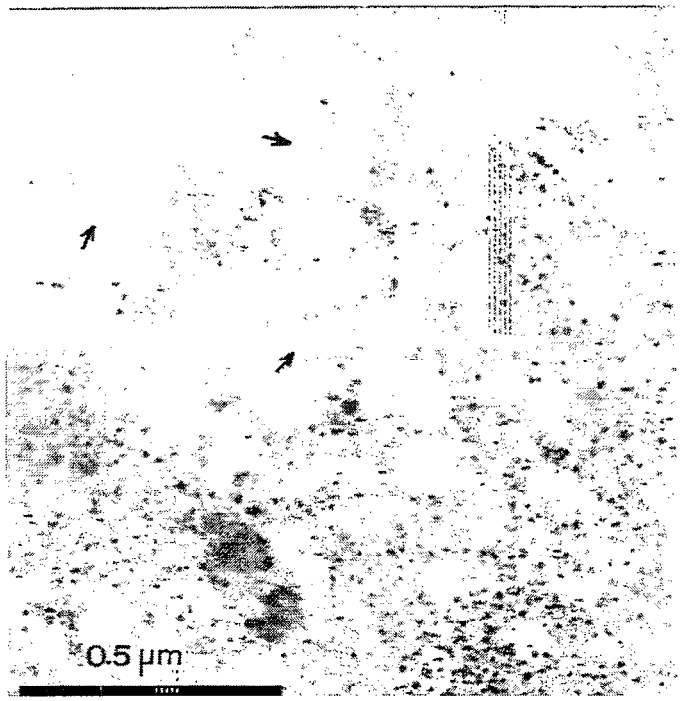


FIG.1 A. Typical graphite and metallic (black dots) debris with enmeshed carbon nanotubes (arrows).

FIG.1B. Multiwalled nanotubes grown on silicon substrate (arrows).

FIG.2A. Individual Caco-2 cell treated with antibody- functionalized nanotubes (purple dots) to block gClq-receptor sites prevented Listerial bacteria (arrows) from entering the cell in that region. 1000X oil.

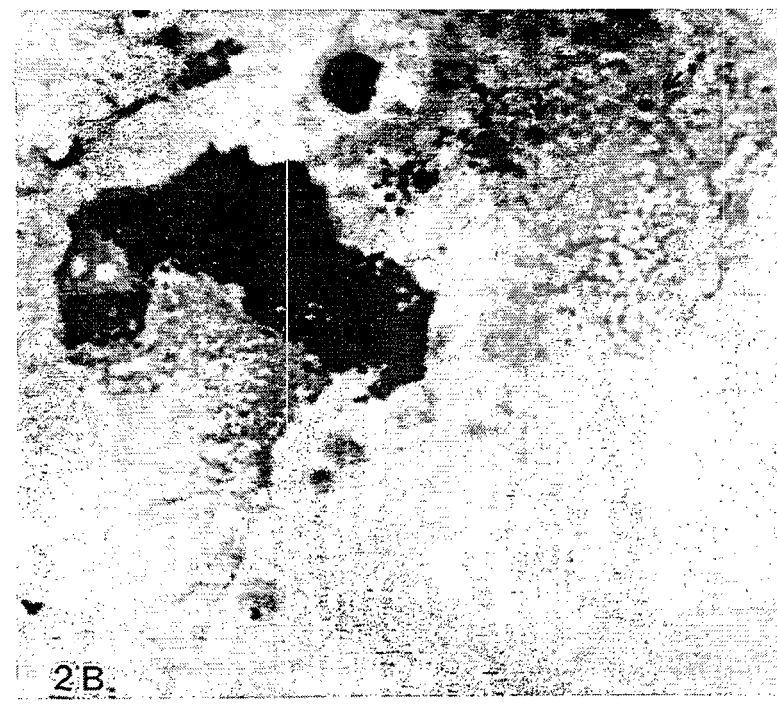


FIG.2B Two Caco-2 cells treated with antibody functionalized nanotubes (dark dots). One cell shows specific cluster binding (capping), with Listeria bacteria (red) and their polymerized actin(red lines) tails in the cytoplasm without the nanotubes. The cell on the right is filled with Listeria, but has two clear areas adjacent to the 2 antibody –nanotube clusters (arrows). 1000X oil

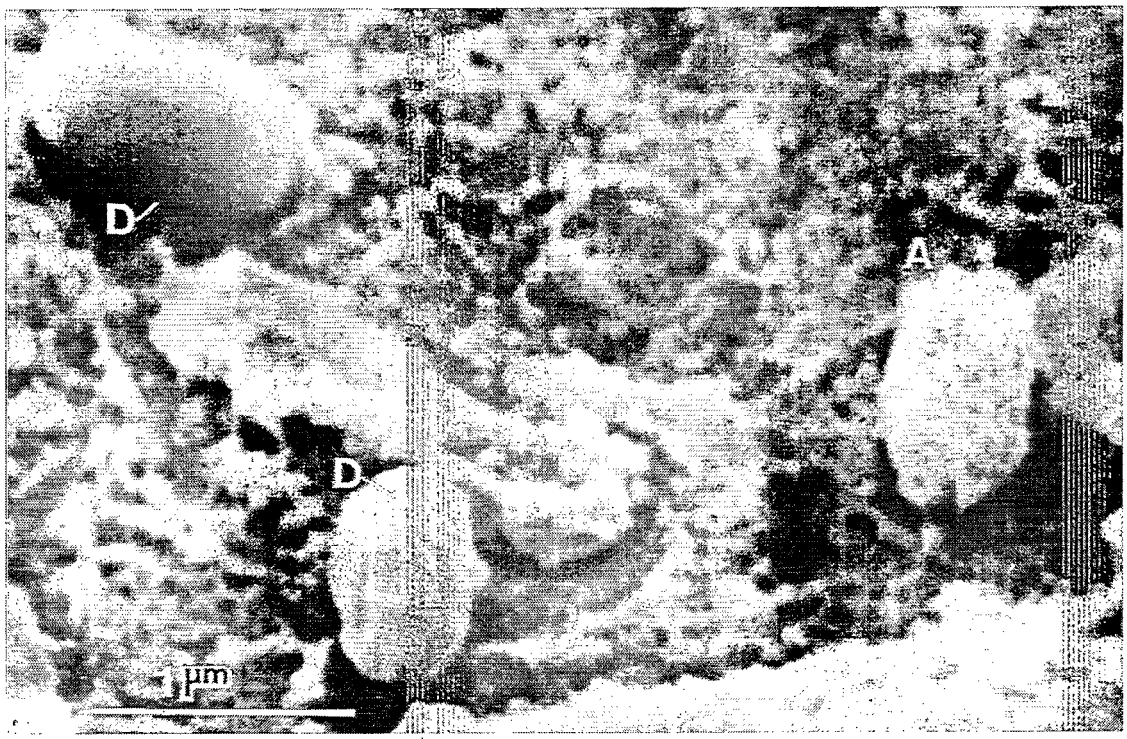


FIG.3A. Field emission SEM image of dormant (D) and activated (A) Bacillus spores. The activated spores have surface attachment appendages on the outer membrane that will be characterized in the nanotube attachment studies. 5KV

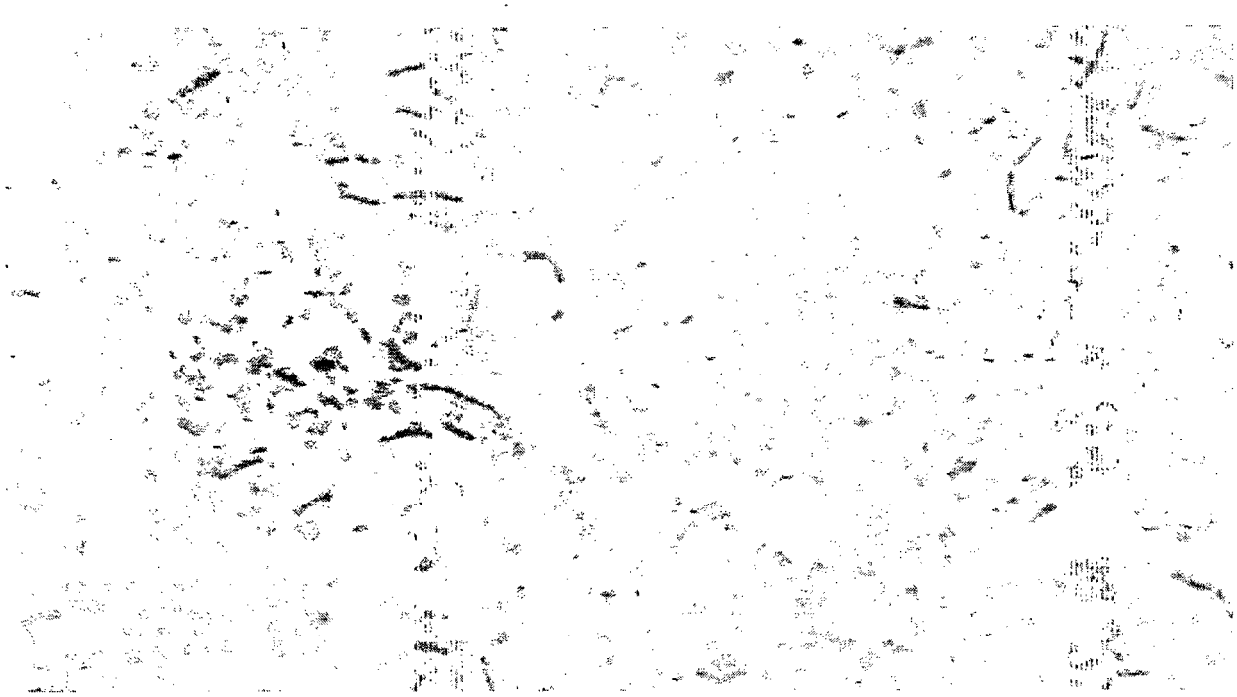


FIG.3B. Light micrograph of malachite green – safranin stained Bacillus spores isolated and grown for attachment experiments with cells and AFM nanotube adhesion part of study. 1000Xoil

Self-Organized Nanoparticles for Probing Charge Transfer at Metallic/Organic Interfaces

Myron Strongin *01-86*
J. Tu
S. Maslov
S. Feldberg
V. Perebeinos

PURPOSE:

This proposal is concerned with using self-assembled nanoparticle arrays to study charge transfer mechanisms in organic molecules as well as in metal-organic interfaces.

APPROACH:

The approach is to form self-assembled arrays of metal nanoparticles by evaporation onto substrates held at 10K. Organic molecules are then quench-condensed onto the surface, and changes in the DC conductivity and optical properties are measured. These changes will elucidate the charge transfer mechanisms in organic molecules and between metal-organic interfaces. At the present time we have tried initial DC transport measurements and the first optical studies of organic molecules (decanethiol) on gold clusters at 10K. The possibility of carrying out the DC transport and optical measurements in a field-effect transistor (FET) configuration is under active consideration. Such a capability will lead to a way of putting charges on the clusters and lead to new areas of research. As usual, initial experiments have indicated some of the difficulties and high risk in making cluster/molecule connections, but these can be overcome and interesting results are already beginning to emerge.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, construction and testing of a new ultra-high vacuum chamber for combined transport and optical measurements were carried out, and presently the chamber is in its final stages of mechanical and optical construction. Two Stony Brook undergraduate students are dealing with interfacing this chamber to the Bruker FTIR IR spectrometer. In FY2001, analysis was also made of data on ultra-thin Au films deposited on amorphous Ge. This data seems to indicate a dielectric anomaly in the 2nm regime, where the film goes through a percolation transition from the insulating to metallic state.

In FY 2002, besides dealing with the new chamber, transport studies have been made of Au clusters (with and without decanethiol) in a rapid "turn around" diffusion pumped system. One of our standard flow cryostats was used to change the temperature between room temperature and 10K. Most of the gold films were deposited onto substrates held at 78K. The system is equipped with a quartz crystal oscillator rate monitor for thickness measurements, and a standard four-probe technique is used for the resisitivity measurements. One somewhat surprising conclusion from the results is that the properties of ultra-thin Au films, even without organics, are not well understood. Rather than seeing a distribution of isolated grains with activated conductivity, we always see features characteristic of correlated behavior, and in the 10 Megohm regime we see features characteristic of a Coulomb glass. This state of matter is of great interest in itself; however, we surprisingly saw little effect due to decanethiol. At the present time this can apparently be explained by the fact that there is only one sulfur group on the thiol

molecule we used. Since the sulfur group is crucial in the linkage to Au clusters we think another sulfur group is needed, and this is the reason for the small changes in resistivity. It is somewhat surprising that even capacitive effects are small, and these experiments are still ongoing. The same conclusion is reached in the recent optical study of decanethiol on gold clusters where little change was observed in the optical properties of Au film after the decanethiol molecules were quench-condensed on it.

The major accomplishments to date are the design and construction of the optical chamber that will actually allow measurements of both the reflectivity and transmission of ultra-thin films be carried out in ultra-high vacuum. We have also modified our optical setup to allow organic molecules to be quench-condensed *in situ* onto suitable substrates held 10 K.

SPECIFIC ACCOMPLISHMENTS:

A paper is under preparation concerning the phase transition that was found in both ultra-thin Au and ultra-thin Pb films. The size of the grains in these systems is of the order of 1 nm, and this is a regime that has not been studied optically. This type of system with grains near 1 nm is of great interest in our studies of the effects of organics.

LDRD FUNDING:

FY 2001	$46,504
FY 2002 (budgeted)	$50,000
FY 2003 (requested)	$50,000

Charge Transfer on the Nanoscale: Theory

Marshall D. Newton *01-87*

PURPOSE:

The objective of this project is to demonstrate the feasibility of calculating the energetic and electronic structural characteristics needed to model charge transfer dynamics in extended (tens of angstroms) oligomeric systems comprised of organic or organometallic building blocks. The work is exploratory, in comparison with current techniques typically employed for chemical systems of modest size, in that it 1) includes a full account of many-electron and final- as well as initial-state effects, and 2) is tested by application to quite large-scale molecular assemblies ($\gtrsim$ 100 atoms and $\gtrsim$ 300 electrons, including transition metal atoms), so as to assess limitations due to issues of convergence and numerical precision. The results will be of value in critically evaluating the merits of common mean-field approaches which generally suppress state-specific and multi-particle effects. Success in this venture will be valuable as an adjunct to future BNL plans for a nanoscience center.

APPROACH:

The massive current interest in designing and characterizing nanoscale conductive junctions constitutes a major opportunity for exploiting the power of contemporary techniques of computational quantum chemistry and electron transfer theory in modeling the requisite molecular properties governing the overall conductive behavior.

This project specifically deals with evaluation of long-range electronic coupling of localized donor and acceptor sites, the modulation of such coupling by vibrational motions (electron-phonon coupling), and the sensitivity of the coupling (and hence, the conduction mechanism) to tuning of relevant energy gaps (e.g., by chemical substitution).

The theoretical models are implemented computationally using a variety of many-electron quantum mechanical techniques, including configuration interaction and density functional (DF) methods. Models for charge transfer kinetics employ the Golden-rule dynamical model or suitable semiclassical extensions. In collaborative work with Dr. Vasili Perebeinos (BNL Physics), model Hamiltonians based on results from DF calculations are being formulated for study of vibronic coupling in extended conducting junctions based on Green Function methods.

TECHNICAL PROGRESS AND RESULTS:

FY 2001

A systematic study was completed for long-range electronic coupling in a family of homologous systems of generic type DSA (donor, spacer [i.e., "wire"], acceptor), where the sensitivity of coupling was quantitatively characterized with respect to chemical substitution (on both D, S, and A units), molecular conformation (oligomer torsion angles), electronic spacer type (saturated vs unsaturated) and length (number of spacer units), donor electronic state type (of crucial importance for quasi-degenerate transition metal complexes), and charge carrier type (electron vs hole). The completion of these calculations constitutes the first significant milestone for the project. The quantitative measures of coupling sensitivity have important implications for assessing the charge transfer propensities of alternative molecular assemblies, and for design of new systems.

FY 2002

Building on the progress in FY 2001 (focussed primarily on electronic structure), the FY 2002 work will increasingly deal with electron-phonon coupling, elucidating quantitatively the role of specific vibrational or torsional modes of conductive assemblies in modulating electronic coupling and energy gaps separating donor/acceptor manifolds from those of the molecular spacers. Model Hamiltonians (parameterized using full electronic calculations) and molecular dynamics simulations (MD) are expected to play a significant role in the computational studies.

SPECIFIC ACCOMPLISHMENTS:

Obtained funding for a DOE proposal "Charge Injection and Transport in Nanoscale Materials" funded for the period FY 2001-2004.

Refereed Publications

Adiabatic Interfacial Electron Transfer over 26 Å through Oligophenylenevinylenes, H.D. Sikes, J.F. Smalley, S.P. Dudek, A.R. Cook, M.D. Newton, C.E.D. Chidsey, and S.W. Feldberg, *Science* **291**, 1519-1523 (2001)

Electronic Coupling of Donor/Acceptor Sites Mediated by Homologous Unsaturated Organic Bridges, Marshall D. Newton, *Advances in Chemistry Series* (in press)

LDRD FUNDING:

FY 2001	$43,063
FY 2002 (budgeted)	$55,000
FY 2003 (requested)	$55,000

Charge Transport Through Dye-Sensitized Nanocrystalline Semiconductor Films

Bruce Brunschwig *01-88*

PURPOSE:

The conversion of solar energy into electricity has been accomplished primarily by semiconductor photovoltaic devices. Over the past few years a new type of solar conversion device has been developed based on liquid junction photovoltaic cells. The cells make use of dye-sensitized charge injection into nanocrystalline TiO_2 films (see figure 1). While the initial charge injection step is very fast, the subsequent conduction of the charge through the TiO_2 is much slower. The proposed research focuses on the nature of charge conduction through TiO_2 particles.

APPROACH:

A range of studies that focus on charge transfer in nanocrystalline systems are being undertaken. First, electroabsorption (Stark) spectroscopy will be used to characterize the initially formed charge transfer state of the dye-adsorbed system. Secondly, we will develop systems that have both an electron donor (dye) and an acceptor attached to a single nanoparticle. We will study the charge conduction from the excited donor through the particle to the acceptor on nanoparticles suspended in solution. No work of this type has been reported.

The study of charge transfer phenomena on the nanoscale is part of the BNL initiative to develop new research programs in the size region between the molecular and the micro (or the region where bulk materials begin).

The research proposed will characterize the dynamics of charge flow from an electron donor through a nanoparticle to an electron acceptor and the back transfer. Two types of dye sensitization have been reported. One involves direct injection of the charge from the dye to the nanoparticle. The second involves indirect injection in which an excited state of the dye molecule is initially formed that then injects charge into the particle. The direct injection mechanism results from excitation in a new absorption band that is formed when the dye is attached to the particle while no new absorption features are present in the indirect mechanism. Stark spectroscopy affords a means of characterizing the charge transfer state: determination of the distance of the initial charge transfer and the changes in the dipole moment and polarizability between the ground and initially formed Franck-Condon state. For the direct injection mechanism this should yield information about whether the Franck-Condon state is part of the conduction band of the particle or localized on an individual titanium metal center. For the indirect mechanism it will allow one to assess whether the excited state of the dye has different properties when it is free in solution or attached to the nanoparticle. The Stark spectroscopy studies will measure spectra for a number of different donors (both direct and indirect) and for nanoparticles freely suspended in solution and attached in nanocrystalline films.

Another area of research will focus on measurements of the rates of charge transfer reactions mediated by nanoparticles. Systems in which both a donor and an acceptor molecule are attached to the particle will be studied. The rates of charge injection from a dye into the nanoparticle and back have been measured by others and the rates are described either by second

order kinetics or by a multi-exponential decay. The measurements suggest that the injected electron never moves a significant distance from the point of the dye attachment. We propose to attach both a donor and an acceptor that is positioned so that the charge will have to undergo a number of jumps on (or in) the particle to reach the acceptor. This will allow us to characterize the dynamics of charge motion through the nanoparticle.

We have begun work with Dr. G. Meyer's group at Johns Hopkins University and Dr. Elena Galoppini's group at Rutgers-Newark. Other collaborations with Dr. David Thompson at Memorial University Newfound, Dr. Edward Castner at Rutgers-New Brunswick, and Dr. Stanislaus Wong at SUNY Stony Brook are being developed. Within BNL collaborations on nanoscale research are underway with Dr's C. Creutz, N. Sutin, E. Fujita, J. Hanson.

TECHNICAL PROGRESS AND RESULTS:

FY2001

1. Stark Spectra of $Fe(CN)_6$–TiO_2: The first Stark spectra of a dye attached to a nanoparticle that exhibits a new charge transfer band have been collected and interpreted (see figure 2). The charge transfer distance determined from the spectra is 5 Å and very closely matches the distance between the Fe center and the Ti^{iv} that is coordinated to the nitrogen end of one of the CN ligands of the ferrocyanide complex. This result is the first to show conclusively that the direct charge injection is to an individual titanium site and not into the conduction band of the particle.

2. Synthesis of TiO_2 nanoparticles: A standard synthetic method that produces anatase TiO_2 nanoparticles of 3 nm diameter has been developed. Specifically, controlled hydrolysis of $Ti(i\text{-}OPr)_4$ (where i-OPr= isopropoxide) in acidic aqueous media was studied. The temperature, pH, and concentration of $Ti(i\text{-}OPr)_4$ solution were found to be important parameters for controlling particle size. The particles were characterized by X-ray powder diffraction and transmission electron microscopy (see figure 3).

3. Postdoctoral associate: Dr. Mikhail Khoudiakov who received his PhD under Prof. Arthur Ellis at the University of Wisconsin – Madison was hired and joined the group in April, 2001.

4. Equipment: A dynamic light scattering (DLS) instrument and a high-speed centrifuge have been purchased. The DLS instrument is used to screen the preparations while the centrifuge is used in the separation. Also an electron-microscope has been reconditioned (under Dr. C. Creutz) and will be used in the characterization of the TiO_2 particles.

FY2002

Stark Spectroscopy: Measurements will be made on dye-sensitized particles in both nanocrystalline films and in solution. Dyes to be studied will include $Fe(CN)_6^{4-}$, $FeL(CN)_4^{2-}$ where L =2,2'-bipyridine type ligands and RuL_3^{2+} and $RuL_2(CN)_2$ systems. The effects of salt (Li^+) concentration, pH and particle size will be studied.

Transient Spectroscopy: Measurements on RuL_3–TiO_2(particle)-A systems will be made, where A will be a methylviologen type of molecule or a metal complex such as RhL_3^{3+}. In ideal cases both the forward reaction that leads to the reduced acceptor and the back reaction from the reduced acceptor will be studied. The effect of Li^+ ion concentration, pH, particle size and

driving force on a given donor-acceptor system will be studied.

Synthesis: Synthetic methods to form both ultra small TiO_2 (<3 nm) and large TiO_2 (>10 nm) will be pursued.

SPECIFIC ACCOMPLISHMENTS:

1. Electroabsorption *Spectroscopy of* $(NC)_5Fe^{II}(CN)Ti^{IV}$ *Systems*. A.. R. Parise, B. S. Brunschwig and N. Sutin. Poster given at the Twenty-Fourth DOE Solar Photochemistry research Conference, Tahoe City, CA, June 3-7, 2001

2. Electroabsorption Spectroscopy of the Dye-sensitized Nanoparticle Systems $(NC)_5Fe^{II}(CN)Ti^{IV}$ A.. R. Parise, B. S. Brunschwig and N. Sutin. manuscript in preparation.

3. Charge Injection and Transport through Colloidal Nanoparticles and Nanocrystalline Semiconductor Films section in *Charge Injection and Transport in Nanoscale Materials A proposal for DOE Laboratory Activities in Nanoscale Science, Engineering and Technology,* C. Creutz 2001.

LDRD FUNDING:

FY 2001	$52,555
FY 2002 (budgeted)	$55,000
FY 2003 (requested)	$55,000

Figures:

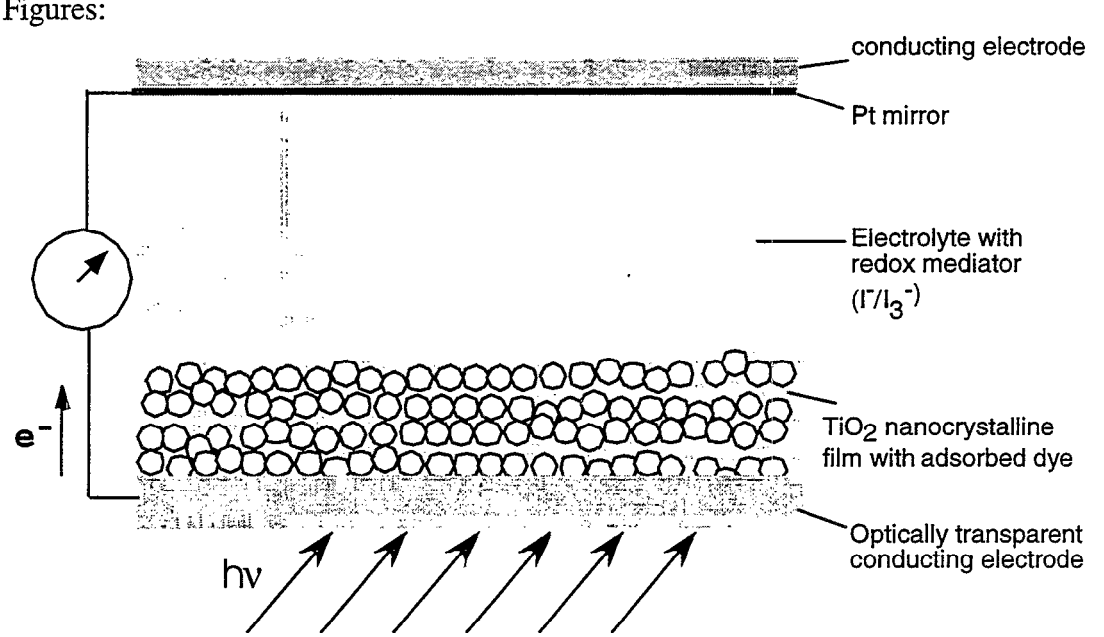


Figure 1. Dye-sensitized Liquid Junction Nanocrystalline Solar Cell (after M. Gratzel).

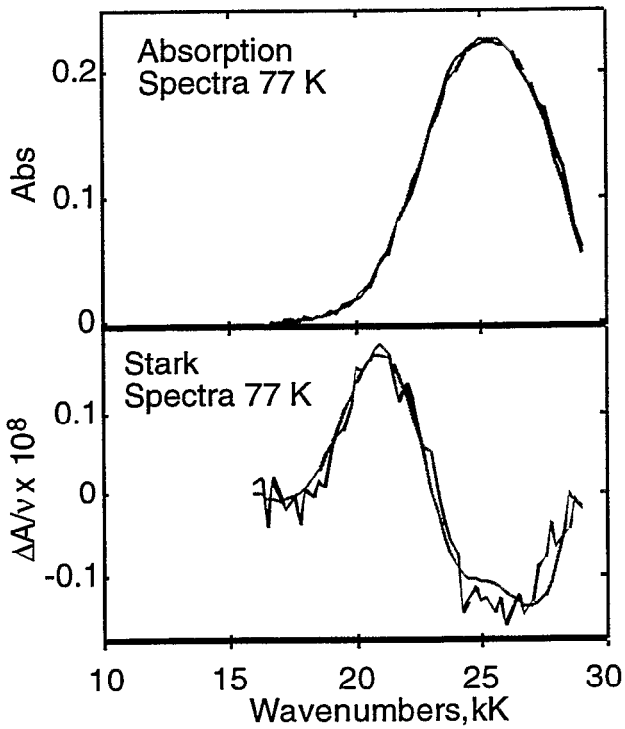


Figure 2. Electroabsorption spectra of $Fe(CN)_6TiO_2$(nanoparticle): Experimental data in blue and fit in green.

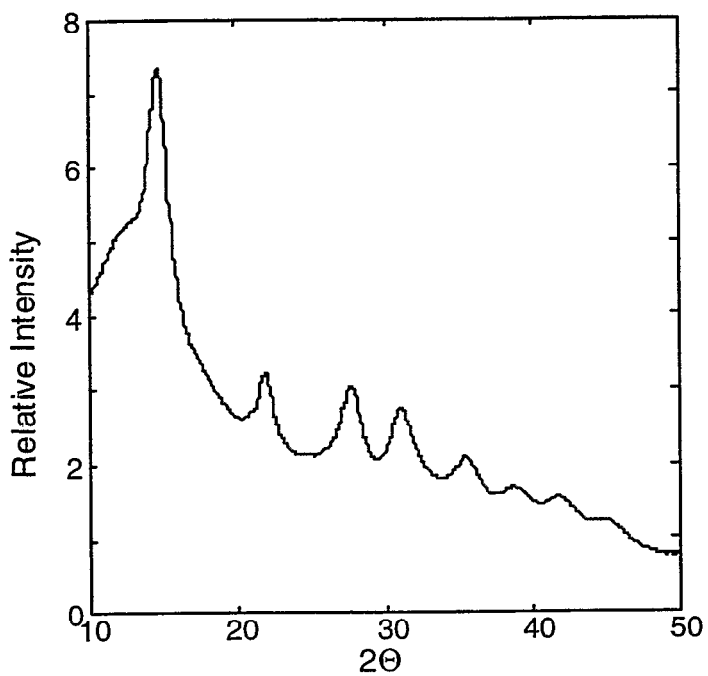


Figure 3. X-ray powder diffraction pattern of ~3 nm diameter TiO_2 nanoparticles.

Magnetic Nanodispersions

Laura H. Lewis *01-91*
C.-C. Kao

PURPOSE:

The objective of this work is to investigate the magnetic properties of well-characterized thin-film systems of two magnetic phases, "magnetic nano-dispersions," with the ultimate goal of understanding the nature and extent of interparticulate magnetic interactions and how these interactions are mediated by the intervening matrix. Qualitative and quantitative results will clarify outstanding questions concerning interactions in magnetic systems from both basic and applied perspectives. This work supports the BNL institutional strategy by constituting a significant portion of the proposed BES Nanoscience Center "Magnetic Nanoassemblies" Thrust Area. Furthermore, the research represents an effort to increase the degree of research collaboration between BNL and SUNY Stony Brook.

APPROACH:

Successful execution of the research first requires the synthesis of multi-phase thin film systems, followed by detailed structural and magnetic characterization. Later-term studies will include advanced x-ray diffraction and neutron and x-ray small-angle scattering to further characterize of the phase constitution, structural scale and magnetic attributes of the systems.

Multi-phase thin film samples are made using the novel technique of reactive ion beam assisted deposition (RIBAD) in the laboratory of Prof. R. J. Gambino at SUNY Stony Brook. The systems MnO + Co and MnO + Pd have been selected for initial synthesis and study. RIBAD uses a focused Ar ion beam from a deposition source to sputter metal atoms from a target onto a substrate surface; simultaneously, a second ion beam from an assist source produces a controlled Ne/O_2 mix beam that combines with the flux of metal atoms to make multi-phase metal and metal-oxide nanometer-sized dispersions.

Basic structural characterization of the films is accomplished by standard laboratory x-ray diffraction and transmission electron microscopy (TEM) to ascertain the phase content, distribution, and dimensional scale. Where warranted, more advanced characterization will be done with high-resolution TEM (in collaboration with Yimei Zhu (BNL) and Perena Gouma (SUNY-SB)) and atomic/magnetic force microscopy. The static (*dc*) and dynamic (*ac*) magnetic responses of the films will be probed with Superconducting Quantum Interference Device (SQUID) magnetometry. Properties to be investigated include uniformity of particle size, interparticulate interactions, and the properties of the blocking temperature.

Magnetic x-ray scattering will be done in collaboration with John Hill (BNL, Physics) to characterize the magnetic profiles of the nanoparticles. These data will then be compared with information obtained from chemical scattering to elucidate the nature of the chemical and magnetic interfaces.

TECHNICAL PROGRESS & RESULTS:

Work on the project began in earnest in April 2001 with the arrival of the post-doctoral researcher assigned to this project, Johan van Lierop. Magnetic characterization was performed on a previously-made thin-film nanodispersion sample of Ni/NiO of

approximately 40 at.% Ni metal and 60 at.% NiO that had crystallite sizes around 6 nm diameter. The magnetic studies revealed the presence of interphase magnetic exchange by the suppression of the Néel and Curie temperatures of the components, as well as by hysteresis loop-shifts that are a measure of the exchange field strength. Furthermore, a strong temperature and maximum applied field dependence for both the coercivity and exchange field strength was present shown in Figure 1. These unique results indicated competition between the exchange interaction of the ferromagnetic Ni and antiferromagnetic NiO nanocrystallites as well as the external-field and NiO surface magnetic coupling interactions.

In addition to the results obtained on the existing films described above, new samples have been synthesized using the RIBAD technique. CoMn samples of 50 nm and 200 nm average thicknesses have been deposited with nominal oxygen contents that ranged from 0%-29% and relative Mn concentrations of 4% and 10%. Initial studies indicated that the deposition parameters yielded the planned relative amounts of Co and Mn. The precise phase constitution of these samples has yet to be determined; however, preliminary resistivity and magnetic measurements confirmed the formation of poor-conductivity oxide phases in the films.

Near-term research goals include previously-described microstructural characterization and initial magnetic studies. It is anticipated that the Magnetic Nanodispersion work will continue under the auspices of the BNL LDRD Program.

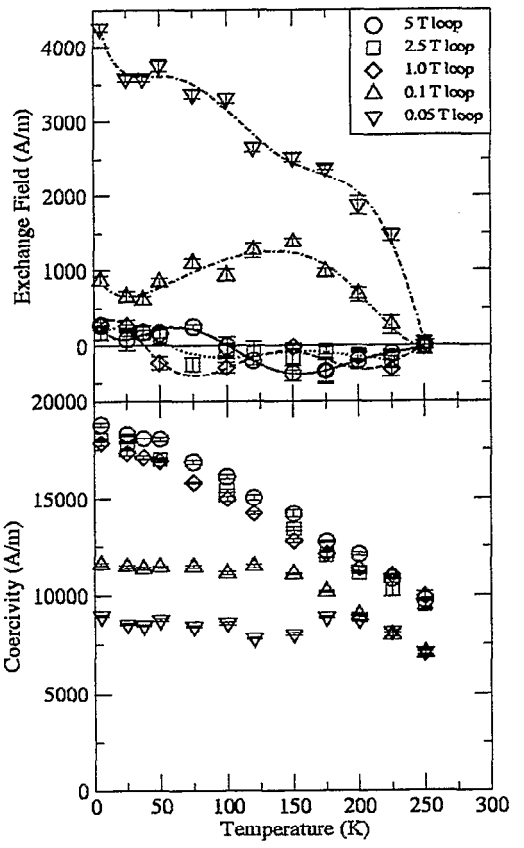


Figure 1: Measured exchange field (top) and coercivity (bottom) from hysteresis loops for the various measuring fields. Lines are guides to the eye

SPECIFIC ACCOMPLISHMENTS:

Peer-reviewed article: J. van Lierop, L.H. Lewis, K.E. Williams, and R.J. Gambino, "Magnetic exchange effects in a nanocomposite Ni/NiO film," *J. Appl. Phys.*, in press.

Poster presentation, "Magnetic exchange effects in a nanocomposite Ni/NiO film" 46th Ann. Conf. on Magnetism & Magnetic Materials, Seattle, WA, Nov. 12-16, 2001.

LDRD FUNDING:

FY 2001	$71,175
FY 2002 (budgeted)	$73,000
FY 2003 (requested)	$77,000

High Resolution Magneto-optical Study of Magnetic Nanostructures, Nano-composite Functional and Superconducting Materials

Qiang Li *01-93*

PURPOSE:

A high-resolution magneto-optical technique will be developed to provide a novel and versatile characterization tool for investigating properties of magnetic nanostructures, nanocomposite functional, and superconducting materials. The success of this technique will greatly broaden BNL's capability to conduct fundamental scientific studies and pursue practical applications of various nano-materials. It is an important element of BNL's strategic effort on building a state-of-the-art nano-material and nano-technology center.

APPROACH:

One of the greatest challenges in the studies of magnetic material is to develop a versatile technique being able to investigate a direct interaction between a small magnetic structure and probes, other than through the stray field produced by the magnetic structures. The magneto-optical effect is one of the very few that provides a direct interaction between the magnetic domain and photons. However, conventional magneto-optical devices have a low spacial resolution due to the diffraction limit of visible light, which is incapable of studying nano-scaled magnetic material.

The proposed high-resolution technique is based on the magneto-optical Kerr/Faraday effect and equipped with a near-field scanning optical probe. This technique allows for a nondestructive and direct observation of changes in local magnetic structures at the nanometer scale. Though some progress has been made in the past few years, it has not yet been demonstrated that such techniques can be operated at low temperatures and under strong magnetic fields with nano-scale resolution. The goal of this project is to explore its feasibility, as well as using this technique to image and study magnetic structures from millimeters down to tens of nanometers. It is clear that this project is one of high risk and high pay-off research, but success will put BNL at the forefront of nano-material research.

Using the magneto-optical effect, we will be able to image, as well as study the phenomena associated with, the nucleation of various magnetic domains (like spin-flop and antiferromagnetic domains), domain wall motion, magnetic interface and antiferromagnetic coupling, etc. Another unique strength of this technique is being able to study the dynamic behavior of magnetic properties and its interaction with nano-scale structural defects simultaneously and nondestructively. The information obtained from the high-resolution magneto-optical technique is extremely valuable and is unattainable with any other existing method, like TEM, magnetic force microscopy, X-ray scattering and diffraction.

TECHNICAL PROGRESS AND RESULTS:

Our approach to the development of this new technique began with building a versatile magneto-optical system, which is robust for daily magnetic imaging of a vast variety of magnetic materials, as well as magnetic flux profiles in superconductors. We will improve the resolution to tens of nanometers by using scanning probes.

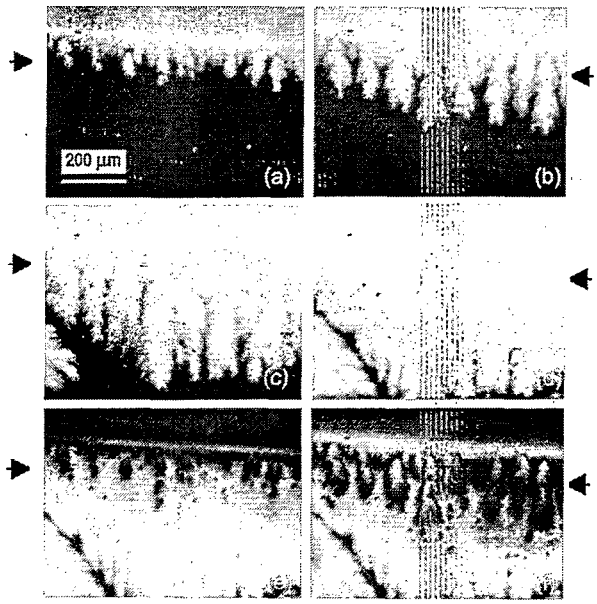
In the first part of FY2001, we purchased and installed an optical microscope with polarizer/analyzer and digital camera with

software for image capture. A new Ph. D graduate student from SUNY at Stony Brook was hired in February 2001 to participate in this project with Janis Corp. We custom-designed (and subsequently purchased) a low vibration, liquid helium continuing flow cryostat with Janis Corp used for temperature control under the microscope. Image capturing and analysis software was tested. In the second half of FY2001, we installed a turbo-pump based vacuum system and successfully tested the temperature control system. We custom designed, winded and tested a copper coil magnet for the cryostat capable of producing up to 1000 Oe magnetic field.

In August-October 2001, we put the system in a milestone test by imaging the magnetic field distribution profile in a newly discovered MgB_2 superconducting film. It was a remarkable success, where the stability and reproducibility of this home made magneto-optical system surpassed all the performance parameters we had expected from an optical microscope. We found that our instrument can be operated continuously from 350 K down to 2 K and under magnetic field up to 1000 Oe with excellent stability.

The following figures illustrate our magneto-optical study of a *c*-axis oriented MgB_2 film. We observed a global penetration of magnetic vortices dominated by complex dendritic structures entering the superconducting region from the edge of the film. We suggest that this behavior was due to a flux jump in MgB_2 superconductors. From these magneto-optical images, we were able to obtain various important properties of superconducting MgB_2, such as mass anisotropy, critical current density as a function of temperature and field, and full penetration field.

Other magneto-optical studies of clustering of magnetic dispersions (e.g. in Ni-NiO), domain wall movement and magnetic phase transition



Figures show magneto-optical images of flux penetration and trapping (image brightness represents flux density) into the virgin (zero-field-cooled) state of superconducting MgB_2 thin film (arrows indicating the film edge) at 5.5 K. The respective images were taken at external fields (perpendicular to the film) of ~ 50, 150, 300, 450, 200, and 0 Oe during a field increasing and decreasing cycle. At ~ 450 Oe, full penetration was reached, as shown in figure (d).

in various materials had been started using the same instrument that we had just built. We also stated designing the scanning optics with magneto-optical analysis based on NSOM.

SPECIFIC ACCOMPLISHMENTS:

A presentation was given at the Material Research Society 2001 Fall Meeting entitled, "Superconducting and Microstructural Properties of MgB2/Mg Nano-Composites." Two papers under final preparation are: 1) Superconducting and Microstructural Properties of MgB2/Mg Nano-Composites, 2) Magneto Optical Studies of Superconducting MgB2 and MgB2/Mg Nano-Composites.

LDRD FUNDING:

FY 2001	$32,748
FY 2002 (budgeted)	$46,000
FY 2003 (requested)	$50,000

Quantum Structure Fabrication and Characterization using Advanced Transmission Electron Microscopy

Yimei Zhu *01-94*
M. Malac

PURPOSE:

The ability to fabricate and to characterize tailored nanometer-scale structures is of significant importance to the science and technology of the new century. The purpose of this project is to set up a nano synthesis system based on electron lithography in a transmission electron microscope (TEM) and to contribute to our fundamental understanding of structure behavior and physical properties at extremely small length scales. We first aim at fabricating magnetic quantum particles with sizes in the order of 10 nm. We utilize advanced nano-probe TEM techniques including in-situ heating, cooling, variation of magnetic fields around the particles and electron holography to measure local magnetic induction distribution. The use of TEM allows us to simultaneously obtain information on crystal structure and magnetic and electronic structure of nano-scale particles.

APPROACH:

A first step in the quest for urgently needed experimental data is a reliable method for fabrication of magnetic structures on a few nanometer length scale. From a more practical point of view such a fabrication method is essential for prototyping and testing of new devices. The need for a well-defined wide variety of shapes of such structures as well as capability to determine the position of the structures suggests the use of lithographical techniques rather than chemical and self-assembly methods.

We aim at using the TEM for fabrication of nanometer size structures suitable for electron-holography experiments. The most restrictive requirement posed by the electron holography, in addition to the minute dimensions of the studied structures, is the necessity of uniform, amorphous, and thin (less than about 10 nm) substrates.

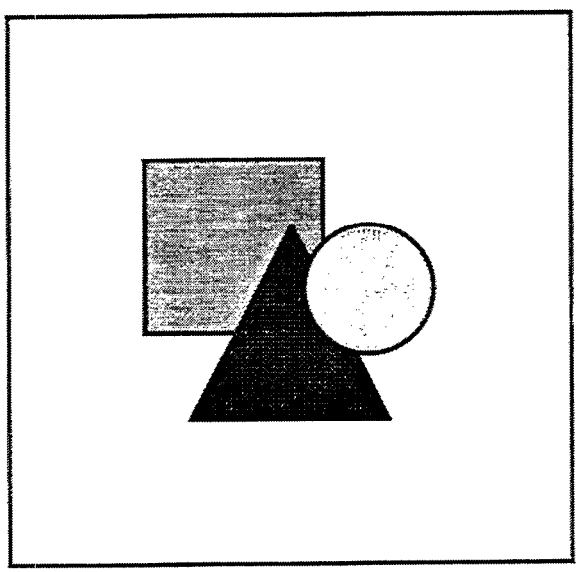
We plan to continue to search for a precursor material suitable for direct in-situ writing of transition-metal structures. We plan to expand our search towards patterning in TEM and dry etch of high-quality transition-metal films prepared in our new ultra high vacuum (UHV) electron-beam deposition system.

Scanning tunneling microscope (STM) is an alternative tool for fabrications on the atomic scale, but is too slow for fabrication of structures with characteristic dimensions in the order of several nanometers. Additionally, the analytical capabilities of STM and the resolution of magnetic-field mapping using atomic force microscope (AFM) are far inferior to the capabilities of TEM.

TECHNICAL PROGRESS AND RESULTS:

Within less than a year, we have designed and built a UHV system and set it up in a semi-clean laboratory prepared for the system. It is equipped with two electron-beam sources which can be operated simultaneously allowing for growth of binary alloys with precise control over the film composition. Each of the electron-beam sources has three separate pockets. The whole assembly allows us to deposit up to six layers without the need of braking the vacuum. The system is capable of growing

epitaxial layers. A reflected high-energy electron diffraction (RHEED) system will be installed in the future to monitor the film growth. Figure 1 shows the actual view of the system.



The UHV system is currently operational although further improvement is needed. We have succeeded with TEM in-situ fabrication of < 10 nm cobalt particles on 10 nm-thick amorphous carbon substrate. We, however, have not yet achieved the desired level of control over the shape of the individual cobalt particles.

SPECIFIC ACCOMPLISHMENTS:

"Exposure characteristics of Cobalt Fluoride (CoF_2) self-developing electron-beam resist on sub-100 nm scale" by M. Malac, M. Schoefield, Y. Zhu, and R. Egerton. J. of Applied Physics (submitted)

LDRD FUNDING:

FY 2001	$89,486

Ultrafast Power Dependent Dynamics of CdS(Se) Quantum Dots in Glass

Dan Imre *01-97*
M. Brell
J. Zhang

PURPOSE:

Semiconductor quantum dots (QDs) are nanoparticles that exhibit novel optical and electrical properties due to confinement of their charge carrier wave functions in three dimensions. Confinement phenomena become important when the radius of the semiconductor nanoparticle becomes equal to or smaller than its Bohr exciton radius. The most characterized and well-understood confinement phenomenon is the blue shift of the ground state absorption, due to exciton confinement, analogous to the quantum-mechanical particle-in-a-box. Although the effects of confinement on linear absorption are well understood, its two-body dynamics effect such as exciton-exciton recombination processes are poorly investigated despite the fact that these recombination processes have important implications for the integration of QDs into electro-optical devices.

Several studies of the transient absorption of semiconductor QDs have been reported previously. The transient absorption signal may carry contributions from band edge carriers, trapped carriers, and/or solvated carriers. The studies described here aim to unravel the electronic relaxation pathways and assign, with a focus on determining which one is responsible for the power-dependent, ~ 1.5 picosecond decay that we observed previously.

We have previously reported on power dependence studies of ultrafast electron dynamics in aqueous CdS QDs. Particles of vastly differing surfaces, sizes, electronic structures, and solvents all show a fast power dependent 1.5-4ps decay component whose amplitude increased with power and a longer decay on the order of 50ps. The rapid decay was assigned to exciton-exciton annihilation, which under high intensity is dominant where multiple photoexcited charge carriers are created in each quantum dot leading to trap state saturation and an accumulation of band edge excitons. It was also shown that the power dependent decay is only weekly dependent on surface, size, and electronic structure. In the present study, we have used two different commercial samples of CdS(Se) nanoparticles embedded in glass, each with different sulfur-to-selenuim ratios, to study the nature of the high power species and the changing decay time constant. We have been able to achieve even higher excitation powers than the previous studies and have found that the decay time constants can be fit with equal values but varying amplitudes.

APPROACH:

The CdS(Se) samples were obtained commercially from Schott glass. The samples were GG495 and OG515. The numbers correspond to the cutoff wavelength for transmission; hence, GG495 begins absorbing light strongly at 495 nm and and OG515 at 515 nm. These different values are obtained by changing the ratio of sulfur-to-selenium in the samples. The dynamic measurements were performed using a pump-probe scheme with a regeneratively amplified, mode-locked femtosecond Ti-sapphire laser. Briefly, pulses of 40 fs duration with 5 nJ/pulse energy at a repetition rate of 100 MHz were generated and amplified in a Ti-sapphire regenerative amplifier using chirped-pulse amplification. The final output pulses

obtained were typically 150 fs with pulse energy of 350 μJ, centered at 780 nm at 1 kHz. The amplified output was doubled in a 1 mm BBO crystal to generate 30 μJ/pulse of 390 nm light, which was used as a pump source to excite the glass samples. The remaining fundamental was focused into quartz to generate a white light continuum, and the desired probe wavelength was selected by using an interference bandpass filter.

TECHNICAL PROGRESS AND RESULTS:

The static absorption and fluorescence spectra of GG495 and OG515 are shown in Figure 1. The absorption spectra, Figure 1a, shows absorption onsets of 495 nm for GG495 and 515 nm for OG515. The fluorescence spectrum, Figure 1b, of sample GG495 shows some band edge emission around 480-505 nm as well as an emission peak at 528 nm. Sample OG515 also shows the 528 nm emission peak, but not as much band edge emissions as GG495. Both samples also exhibit deep trap emission seen in the 560-625 nm region. The overall quantum emission yield is less than 1%, indicating that the majority of charge carriers relax non-radiatively.

Figure 2 shows a comparison of the transient absorption signals of samples GG495 and OG515 under the same experimental conditions and excitation power of 8μJ/pulse. Figure 2a shows the 0-12 ps window, while Figure 2b extends to 120 ps. It can be seen that within signal-to-noise ratio there is no observable difference in the dynamics between the two samples. The dynamics are clearly similar for these particles even though they display different absorption and emission spectra.

The dependence of the 790 nm transient absorption of sample GG495 on the 390 nm pump power is shown in Figure 3. Note that three different time scales are shown. The fitting (not shown) consisted of a pulse width limited rise (~250 fs) and a double exponential decay, with time constants of 1.5 ps and 50 ps, plus an offset. The offset and the 50 ps decay time constants, which were determined from 0-600 ps scans, were held constant for all fits. Time constants were also held constant in order to assure that they fit both the 0-12 ps and 0-120 ps scans and to determine the relative amplitude changes of the fast components with respect to power. Figure 4 shows the 0-12 ps scan with the transient absorption signals normalized to better show the changing amplitudes of the decay components. Note that the lower the power the less the fast component contributes to the signal. The dependence of the 790 nm transient absorption of sample OG515 on the 390 nm pump power is shown in Figure 5. Figure 6 shows the 0-12 ps scan with the transient absorption signals normalized to better show the changing amplitudes of the decay components. Again, note that the lower the power the less the fast component contributes to the signal.

The slower - tens of picosecond decay was shown to be power independent and can be assigned to the trapping of charge carriers which is consistent with the time-resolved fluorescence studies reported by others.

In a previous experiment, nanosecond fluorescence showed that there was an accumulation of band edge excitons as the photoexcitation power increases. Thus, at high power, a new decay mechanism may arise due to exciton-exciton interactions. Two excitons may interact, where one exciton recombines transferring its energy to the other. This decay mechanism is known

as exciton-exciton annihilation, which is most likely responsible for the power-dependent, 1.5 ps transient absorption decay we have observed, consistent with recent studies showing the excitonic fluorescence peak to be independent of the surface. A power-dependent excitonic bleach has also been observed in $Zn_xCd_{1-x}S$ QDs, where the fast, power-dependent decay time constant of the bleach decreased from 1.3 to 0.8 ps as the power was increased. This decrease of the decay time constant is consistent with our previous study of aqueous CdS QDs and with the second-order exciton-exciton annihilation mechanism.

All of the ultrafast transient decays reported here for CdS(Se) QDs in glass exhibit a 1.5 picosecond exponential decay component whose amplitude increases with laser power, a slower ~50 picosecond component and an absorption offset which persists beyond 600 picoseconds. The power-dependent decay has been assigned to band edge excitons, which accumulate under high power excitation following trap state saturation. The excitons decay primarily via an exciton-exciton annihilation mechanism.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2001	$87,349
FY 2002 (budgeted)	$90,000
FY 2003 (requested)	$95,000

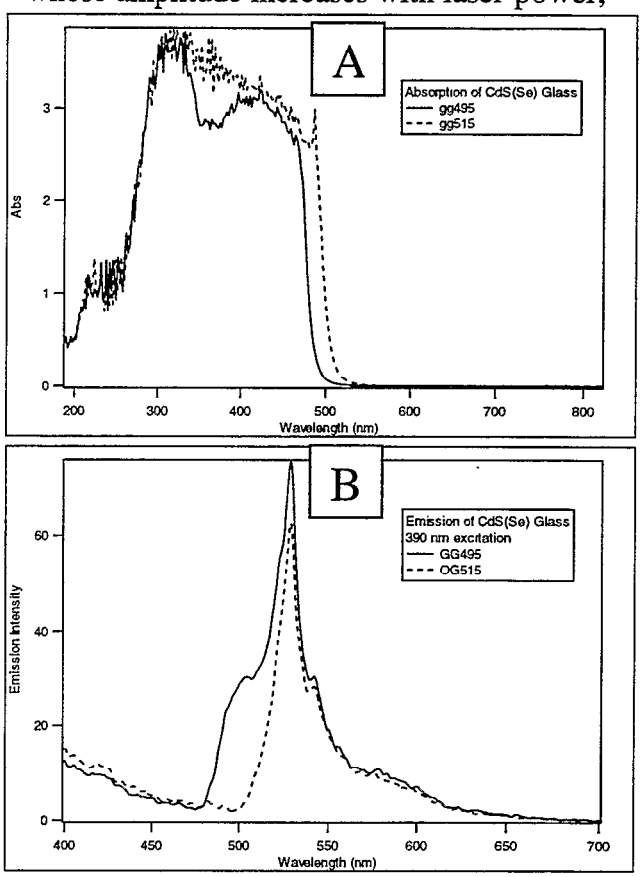


Figure 1: (A) Absorption spectra of GG495 (solid line) and OG515 (dashed line). (B) Fluorescence spectra of GG495 (solid line) and OG515 (dashed line)

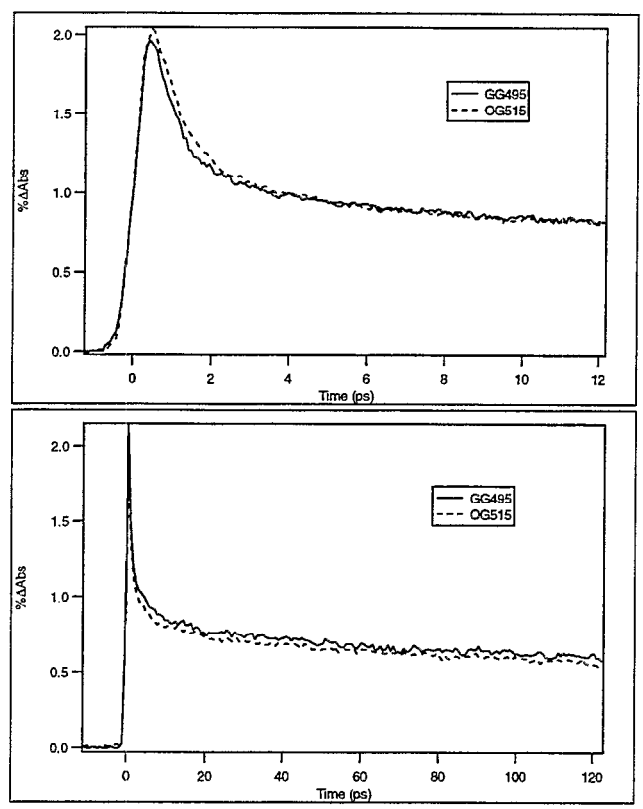


Figure 2: Transient absorption signals at 790 nm of samples GG495 (solid line) and OG515 (dashed line). Note two time scales are shown. The samples were excited with 390 nm pulses at 13 μJ/pulse.

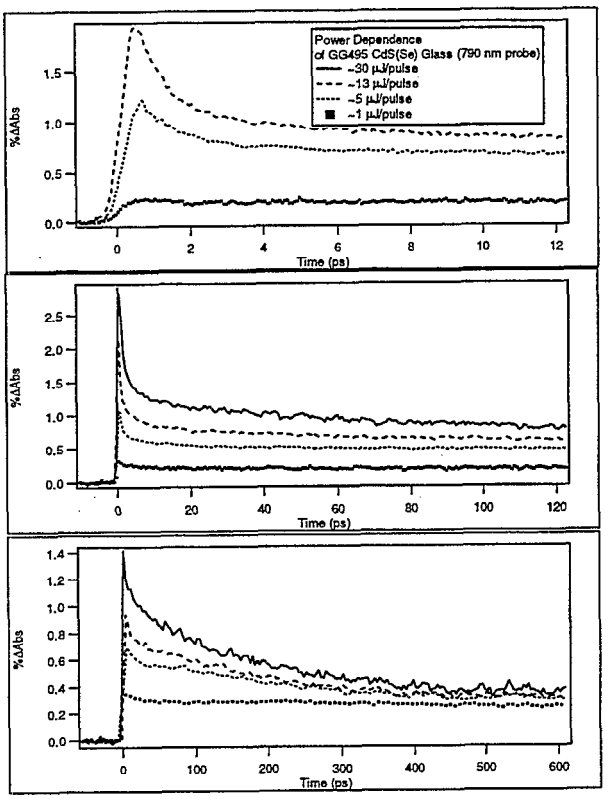


Figure 3: Power dependent transient absorption signal at 790 nm for sample GG495 shown at three time scales. 30 µJ/pulse (solid line), 13 µJ/pulse (dashed line), 5 µJ/pulse (dotted line), and 1 µJ/pulse (squares).

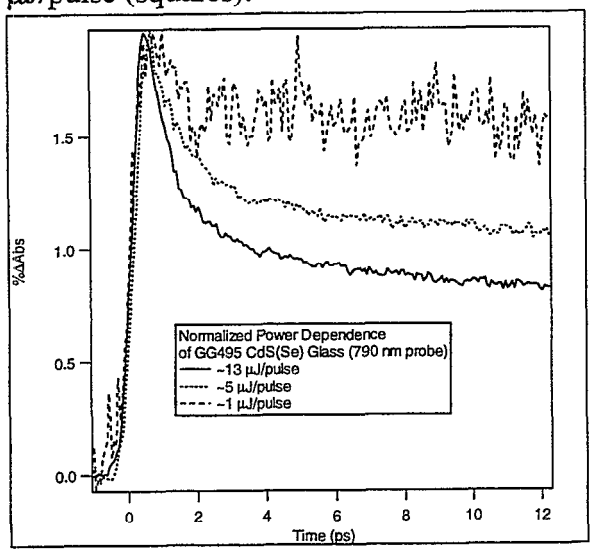


Figure 4: Normalized power dependent transient absorption signals at 790 nm for sample GG495. 13 µJ/pulse (solid line), 5 µJ/pulse (dotted line), and 1 µJ/pulse (dashed line).

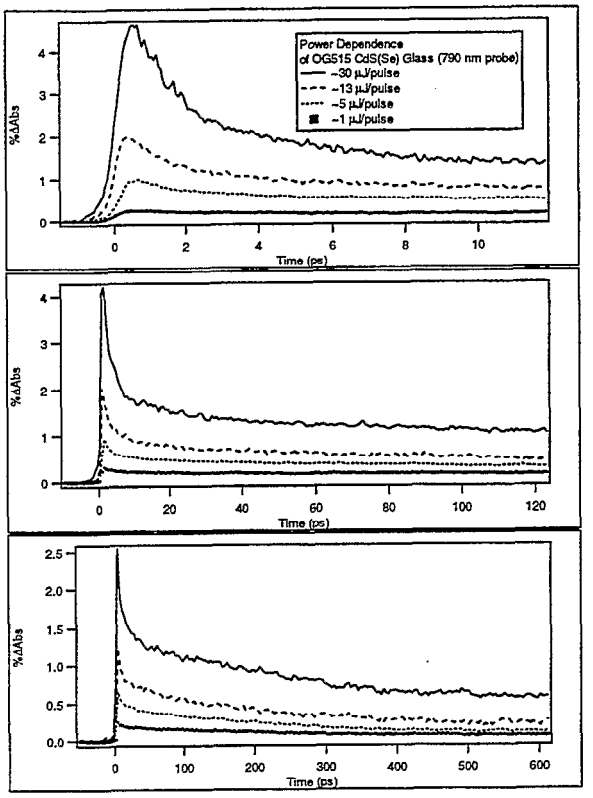


Figure 5: Power dependent transient absorption signal at 790 nm for sample OG515 shown at three time scales. 30 µJ/pulse (solid line), 13 µJ/pulse (dashed line), 5 µJ/pulse (dotted line), and 1 µJ/pulse (squares).

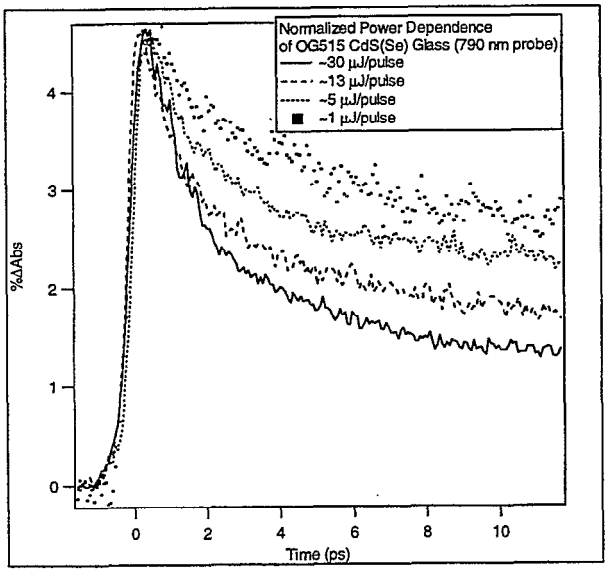


Figure 6: Normalized power dependent transient absorption signals at 790 nm for sample OG515. 30 µJ/pulse (solid line), 13 µJ/pulse (dashed line), 5 µJ/pulse (dotted line), and 1 µJ/pulse (squares).

Appendix A

2002 Project Summaries

Appendix A
BNL FY 2002 Projects

(02-02) Crystallization and X-Ray Analysis of Membrane Proteins
D. Fu (FY 2002 Funding $380,400)

Develop a general approach for crystallization and structure analysis of integral membrane proteins, and to elucidate the structural basis for transmembrane active processes mediated by membrane channels and transporters. Explore new approaches to convert membrane proteins to the equivalents of globular proteins using detergents and other amphipathic reagents and tailor the methodology of general protein crystallization to parameters of integral membrane proteins. The convergence of these two efforts should allow crystallization of membrane proteins using similar principles as for globular proteins.

(02-03) *In Vitro* Investigation of the DNA Double Strand Break Repair Mechanism by Non-Homologous End-Joining in the Context of Chromatin
E. Lymar (FY 2002 Funding $60,000)

Aimed at development of a novel, advanced and physiologically relevant model to study molecular mechanisms of double strand break (DSB) repair *in vitro* to investigate the molecular mechanisms of DNA DSB repair by non-homologous end-joining, which is the major pathway of DSB repair in higher eukaryotes and man. The fundamental questions to be addressed are: (i) What is the molecular mechanisms of DNA damage recognition in the context of chromatin? (ii) What determines factor recruitment to the sites of damage? (iii) What are the factor requirements for efficient DNA repair in chromatin? (iv) What is the nature of chromatin modification required for the DSB repair?

(02-08) Creating a MicroMRI Facility for Research and Development
H. Benveniste (FY 2002 Funding $149,100)

A proposed microMRI instrument to be capable of performing high-resolution anatomical imaging, functional imaging, and a wide variety of spectroscopic studies will serve as a research facility for several investigators whose research requires functional and high-resolution anatomic imaging of rodent (disease) models. Six main research areas have been identified: a) anatomy, b) aging and neurodegenerative disease, c) substance abuse, d) central nervous system (CNS)/inflammation, e) molecular imaging, and f) in vivo imaging of cytolemmal water permeability (aquoporin regulation).

(02-09) Targeting Tin-117m to Estrogen Receptors for Breast Cancer Therapy
K. Kolsky (FY 2002 Funding $80,000)

Synthesize (17α, 20E/Z) tributyltin estradiol and other similar derivatives, and through a structure-activity relationship study of these molecules, select 2-3 successful analogs. Label them with Sn-117m, and test their efficacy for estrogen receptor targeted therapy of breast cancer while sparing the surrounding tissue. Initial tests to be performed in SKBR-5 xenografted nude tumor mice. Extension of the study to synthesize more hydrophilic, long-circulating estrogens by attaching hydrophilic polymers to the steroid molecules.

(02-16) Biomineralization of Actinides: A Mechanistic Study of the Microbial Genesis of Novel and Stable Compounds
A. Francis (FY 2002 Funding $89,000)

Propose to (i) elucidate the fundamental mechanisms of stabilization of soluble actinides (organic- and inorganic-complexes and colloidal forms) by naturally occurring, phosphate and polyphosphate producing micro-organisms; (ii) determine the factors which favor the formation of stable actinide mineral phases by the addition of Ca and other elements; (iii) characterize the nature of the association of actinides with the phosphate mineral; (iv) evaluate stability of actinides with newly-formed phosphate mineral phases; and (v) establish the structure-function relationship with broad application to immobilization of other actinides and toxic metals of interest.

(02-17) Using Mini CO_2-DIAL for Verification and Long-Term Monitoring of Cover Systems
J. Heiser (FY 2002 Funding $125,000)

Seek to develop an optical technique for environmental monitoring that utilizes a Mini-LIDAR (LIght Detection And Ranging) for perfluorocarbon tracer (PFT) detection to determine the flaws (e.g., holes or cracks) and high permeability areas in barriers. Although LIDAR cannot compete with GC methodology in terms of sensitivity, what is needed is not low concentration detection, but rather fast, convenient detection that is fairly robust and can be operated for short periods while remaining dormant for longer periods without adverse behavior.

(02-22) Electrical Systems Reliability
R. Bari (FY 2002 Funding $85,000)

Propose an Electrical Systems Reliability program for the greater New York City area and Long Island. Allow BNL to be established as the regional northeast center for DOE in electrical energy transmission and distribution and as a research organization in this area with an aim of joining or aligning with Consortium for Electric Reliability Technology Solutions. Through an assessment of physical threats and vulnerabilities of multiple feeder contingencies, develop a vulnerability model for a Con Edison distribution network in order to identify these threats to the reliability of the system. From the identification of these configurations, potential modifications to the network, including hardware, monitoring instrumentation, and system control aspects, will be developed, evaluated, and suggested.

(02-24) Liquid Fuel Gasifier for Combustion and Fuel Cells
T. Butcher (FY 2002 Funding $73,000)

Explore the concept of a low-pressure air atomization burner for a liquid fuel, partial oxidation. The key scientific questions addressed are the dependence of soot and deposit formation on the fuel chemical structure and the utility of computational fluid dynamics (CFD) simultations to model the partial oxidation process and guide the design without exceeding computational resources. Use a commercial code (Fluent) which models turbulent, reacting flow with convective and radiative heat transfer. Develop the most appropriate gasification model and the

parameters for radiative exchange. Also propose to explore fuels such as biodiesels whose chemical structure is different enough to mitigate problems in soot and deposit formation.

(02-31) Study of a Power Source for Nano-Devices
M. Lin (FY 2002 Funding $100,000)

Integrate a photo-driven proton pump with nano-devices in order to overcome power transmission problems inherent to such devices (especially free-moving ones). A naturally occurring powerhouse will be used to prove the concept. This natural powerhouse built as part of the nano-device will be driven by solar energy, converting photo-energy into electric potential, thus avoiding transmission of power via direct wiring. The molecular power supply to be tested is bacteriorhodopsin (bR), a purple-colored membrane protein isolated from *H. halobium*, which displays outstanding stability and non-liner optical properties.

(02-42) Ultrafast Nonlinear Spectroscopic Studies of Model Catalytic Surfaces
N. Camillone (FY 2002 Funding $185,000)

Develop new ultrafast nonlinear optical techniques and methods directed at the molecular-level study of the kinetics, dynamics, and structure of organic molecules interacting with a variety of BNL modeled catalytic surfaces in a variable pressure environment. Explore and exploit new ultrafast nonlinear optical techniques and methods to bridge this gap by developing surface science tools and methods which, in terms of complexity, are relevant to a "bottom" up approach to catalysis that can be tested in the same laboratory from the "top" down. Focus specifically on the development of new methods based on two nonlinear optical techniques: second-harmonic and infrared-visible sum-frequency generation.

(02-45) Combined Use of Radiotracers and Positron Emission Imaging in Understanding the Integrated Response of Plants to Environmental Stress
R. Ferrieri (FY 2002 Funding $100,000)

Propose to combine expertise and experience in isotope production and PET imaging with expertise in environmental and stress physiology in plants to develop and validate methods to examine fundamental mechanisms of carbohydrate transport through the phloem, as well as how movement through this transport pathway is affected by environmental perturbations such as water stress. Establish and validate methods for the non-destructive imaging of water and carbohydrate movement in intact plants using short-lived isotopes of carbon, oxygen, and fluorine. By using the short-lived positron emitting isotopes oxygen-15 (half-life: 2 min.), carbon-11 (half-life: 20.4 min.) and fluorine-18 (half-life: 110 min.) combined with Positron Emission Tomography (PET) and phosphor-plate imaging, we have the unique opportunity to visualize quantitatively the assimilation, transport, and disposition of carbon (using $^{11}CO_x$) as well as the movement of water (using $H_2{}^{15}O$ and ^{18}F-fluoride ion in water) in plants exposed to a variety of types of environmental stress under true tracer conditions.

(02-46) Arranging Nanoparticles into Arbitrary Patterns with Optical Trapping
C. Fockenberg (FY 2002 Funding $120,000)

Build an optical trap for multiple nanoparticles that is dynamically adjustable through various methods of beam steering and shaping (i.e., with LCDs, diffractive optics, etc.). Plan to position the nanoparticles into periodic or arbitrary structures of variable dimension, whereby the overall size and shape of the structure can be altered *in situ*, while maintaining trapping. Eventually embed the dynamically trapped nanoparticles into rigid polymers or gel matrices. Ultimately, investigate the possibility of interconnecting the nanoparticles through molecular wires, whereby the connections are established through salt bridges between long-chain thiols absorbed at the surface of these objects in self-assembled monolayers. These structures could be evaluated as practical electronic circuits.

(02-48) Multifunctional Approach for Studying Behavioral and Biochemical Consequences of VOC Exposure
M. Gerasimov (FY 2002 Funding $120,000)

Simultaneously explore the behavioral and neurochemical effects of airborne Volatile Organic Carbons (VOCs) in freely-moving animals. Proposing the acquisition and development of a new state-of-the-art technology (Vaporized Operant Conditioning Chamber) that will be combined with a current *in vivo* microdialysis capability. Expand the current scientific arsenal to include the single most predictive measure of addictive drug behavior, drug self-administration and allow us to specifically identify potential biologic and behavioral consequences to address concerns raised in the community regarding the nature of VOCs and their release from BNL. Determine threshold levels of exposure based on explicit behavioral and neurochemical indices of toxicity. Ultimately, to explore the potential exacerbation of behavioral toxicity when occupational exposure to VOCs is combined with prescribed and/or recreational drug us.

(02-49) Project to Detect pp and 7Be Solar Neutrinos in Real Time: LENS, the Low-Energy Neutrino Spectrometer
R. Hahn (FY 2002 Funding $70,000)

LENS, a Low-Energy Neutrino Spectrometer, incorporates new developments in detector design. It uses an organic-liquid scintillator that is loaded with ~10% of Yb ("YbLS") as the detector. Neutrino capture on 176Yb, with Q=0.301 MeV, produces a β particle, and preferentially leads to excited states in 176Lu that emit γ rays with a ~50 ns lifetime. This β-γ delayed coincidence should reduce random background rates by several factors of ten. Plan to exploit these advances, with the goal of designing and testing prototype *LENS modules*. Position BNL to have a major impact on LENS R&D by (1) improving the chemistry for YbLS production, (2) characterizing optical properties of the YbLS, (3) determining radioactive impurity levels, (4) designing and testing of prototypes.

(02-53) Combined Theoretical and Experimental Study of Crystal Lattice Defects in Complex Transition Metal Oxides
J. Davenport (FY 2002 Funding $40,000)

Combine state-of-the-art first principle theoretical methods for electronic structure and total energy with state-of-the-art quantitative transmission electron microscopy in the study of several well-controlled types of lattice defects in various cuprates and manganites. Use these results to derive more approximate but still accurate theoretical models and their critical parameters for use in the study of less-idealized defects and for the study of systematic behavior in families of compounds. This will contribute to the scientific understanding of complex oxides in general and to their behavior in nanostructures in particular.

(02-55) Chemical Sensors: Immobilization of Organometallic Complexes into Sol-gel Matrices
M. Renner (FY 2002 Funding $82,000)

Use sol-gel technology to immobilize metal macrocycle complexes as sensors for a variety of molecules. By engineering the pore and cavity size, along with varying the macrocycle and metal, we will impart molecular recognition and selectivity. Prepare a series of metal macrocycle complexes in sol-gel matrices which are specifically designed for detection of various molecules. Characterize their chemical and physical properties, screen for molecular recognition, and determine their detection limits. Will lead to a rational design of sensors with enhanced selectivity and sensitivity.

(02-56) Size Dependence of Catalytic Reactivity of Iron Oxide Nanocrystals
S. Wong (FY 2002 Funding $85,000)

Develop a fundamental understanding of intermolecular forces and interactions at the nanometer scale. Accomplished through understanding and rationally designing catalyst materials such as nanosized iron oxide (e.g. individual hematite nanocrystals) by analyzing the efficiency of existing environmentally-significant degradation reactions (e.g., the catalytic decomposition of quinoline in the presence of hydrogen peroxide) as a function of nanocrystal size (~10 nm to 1μ m).

(02-58) Femtosecond Synchronization for Ultra-Short Pulse DUV-FEL Radiation
W. Graves (FY 2002 Funding $135,000)

Using the Deep Ultra-Violet - Free Electron Laser (DUV-FEL), propose to study the production of ultra-short pulses from a high-gain harmonic-generation free-electron laser. Investigate the factors that establish the practical limits on pulse synchronization including: phase control of the linac radio-frequency components, synchronization between the laser systems and the linac, and synchronization of the FEL with auxiliary laser systems. Results will be applicable to multi-color experiments at linac based light source projects such as the Photoinjected Energy Recovery Linac (PERL) and the Linac Coherent Light Source (LCLS).

(02-62) Rapid Wavelength Tunability for the DUV-FEL
B. Sheehy (FY 2002 Funding $135,000)

The Deep Ultra-Violet - Free Electron Laser (DUV-FEL) produces radiation by amplifying a sub-harmonic seed, whereby the output may be tuned "merely" by tuning the seed radiation and the electron beam energy in a stable, synchronous fashion. Each wavelength requires an independent (time consuming) adjustment and checking of the electron beam and seed laser parameters. Experiments demand rapid wavelength scanning, and the purpose of this proposal is to identify all of the problems involved and develop the necessary controls in order to provide agile tunability at an experimentally desired rate.

(02-66) High-Gain Harmonic-Generation at the DUV-FEL
L. Yu (FY 2002 Funding $135,000)

Investigate the design and performance of a high-gain harmonic-generation (HGHG) free-electron laser at the Deep Ultra-Violet - Free Electron Laser (DUV-FEL) facility. Have successfully demonstrated the HGHG FEL in the infrared in an experiment performed at the BNL/Accelerator Test Facility (ATF), and we plan to extend this work into the visible and then down to 100 nm at the DUV-FEL. A key objective is to move the output radiation down to shorter wavelengths, with the ultimate goal of providing an intense, highly coherent source of hard x-rays. It will be necessary to cascade several stages of high-gain harmonic-generation, and we plan to carry out theoretical studies of the cascading process, investigating its potential and sensitivities.

(02-67) Biomineralization: a Route to Advanced Materials
E. DiMasi (FY 2002 Funding $100,000)

Apply state-of-the-art synchrotron x-ray scattering methods to study the interactions between organic molecules and nucleating minerals in a controlled chemical environment. These studies will determine the applicability of several proposed regimes of biomineral growth and transfer of this knowledge to the design of biomimetic composite materials with structural organization on nanometer length scales. Will pave the way for significant advances in the design of composite structural materials, including medical implants.

(02-70) Theory of Electronic Transport in Nanostructures and Low-Dimensional Systems
A. Tsvelik (FY 2002 Funding $135,000)

Focus on the mutual influence of disorder and interactions in low-dimensional mesoscopic systems and devices. Develop a powerful perturbative framework based on the form factor approach to integrable models, and apply it to several simple, but representative, models describing a variety of low-dimensional systems, such as impurities in one-dimensional interacting systems (e.g., quantum wires, carbon nanotubes, and Mott insulators), disordered superconductors, and spectral linewidths in magnetic materials. Expect to employ the form factor approach to integrable models together with a number of theoretical techniques, including mean-field theory, non-linear sigma models, and conformal field theory.

Appendix A
BNL FY 2002 Projects

(02-71) Pressure in Nanopores
T. Vogt (FY 2002 Funding $80,000)

Explore an exciting and novel aspect in nanoscience: by using pressure as a thermodynamic variable to alter the complex and technologically rewarding chemistry occurring within nanopores of zeolites and other micro- and mesoporous materials. The inclusion of intermetallic or metal oxide fragments is known to have unique properties which are different from bulk material and by applying hydrostatic pressure we will alter and tailor these distinctive optical, magnetic, and electrical effects.

(02-84a) Genomic SELEX to Study Protein DNA/RNA Interactions in *Ralstonia metallidurans* CH34 Regulating Heavy Metal Homeostasis and Resistance
D. van der Lelie (FY 2002 Funding $164,000)

Use a SELEX (Systematic Evolution of Ligands by Exponential enrichment) approach to establish a protein-nucleic acid linkage map for *Ralstonia metallidurans* CH34 with emphasis on the interactions of regulatory elements involved in heavy metal homeostasis. Develop an efficient protein (over) expression system for *R. metallidurans* CH34 to overcome potential limitations that are usually related to correct protein folding and modification of heterologously expressed proteins.

(02-84b) Lead Resistance in *Ralstonia metallidurans* CH34
D. van der Lelie (FY 2002 Funding $162,200)

Develop a basic understanding of the newly discovered lead resistance determinant of *R. metallidurans* CH34 and its unique components. Focus on the roles and interactions of the different lead resistance proteins, the structure of their lead binding sites, and functionality of lead resistance protein complexes in natural and synthetic membranes. In addition, the *R. metallidurans* CH34 *pbr* determinant will be compared whith lead resistance determinants of other Ralstonia strains, such as strain DS185 (isolated from Maatheide, Belgium) and LV1, a Ralstonia strain recently discovered as the dominant species at Leadville, Colorado.

(02-85) Design of a *Ralstonia metallidurans* Two-Hybrid Protein System for Studying Signaling Pathways Regulating Heavy Metal Homeostasis and Resistance
S. Taghavi (FY 2002 Funding $166,400)

Develop a Two-Hybrid protein system for elucidating, at the protein level, the signaling pathways that control heavy metal resistance and homeostasis in *Ralstonia metallidurans* CH34. A functional Two-Hybrid protein system in *R. metallidurans* CH34 could also be used to study protein-protein interactions for other environmentally important G+C-rich bacteria, and it will be used in a whole genome approach to establish a protein linkage map (PLM) for the signaling pathways in *R. metallidurans* CH34 that regulate heavy metal homeostasis and resistance. An important challenge will be to translate the complete *Ralstonia* protein-protein interactions revealed by the PLM into computer simulated networks of these interactions to predict the response and adaptation of the organism to different environments.

Appendix A
BNL FY 2002 Projects

(02-86) Ultrafast X-ray Science
S. Dierker (FY 2002 Funding $100,000)

Much of the excitement and scientific demand for a Photoinjected Energy Recovery Linac (PERL) type machine stems from its potential for producing ultrashort (100 fsec) x-ray pulses. Accordingly, we will: (a) produce ultrashort laser pulses synchronized to synchrotron x-ray bunches, a technology central to PERL, (b) pursue high profile, pioneering scientific applications of ultrafast laser/x-ray pump/probe experiments.

(02-88) X-ray Photon Correlation Spectroscopy Studies of Nanostructured Block Copolymers
S. Dierker (FY 2002 Funding $100,000)

Provide an experimental base from which to explore and achieve a theoretical understanding of the short wavelength dynamics by using the technique of X-ray Photon Correlation Spectroscopy (XPCS) to study the short-length scale dynamics of both binary homopolymer blends and also nanostructured. In block copolymer studies, the dynamics of both the highly entangled regime as well as dynamics on length scales comparable to and smaller than the polymer radius of gyration will be investigated in homopolymer blends. The unexplored dynamics in the unentangled regime, as well as the little explored behavior near the critical wave vector for microphase separation will be studied.

(02-91) Fine-Grain Gas and Silicon Detectors for Future Experiments in Nuclear Physics at High Energies
T. Hallman (FY 2002 Funding $100,000)

Development of novel, high-granularity gas tracking devices that may be combined with "hadron blind" tracking ability. Also of importance is the application of the next generation of high-resolution silicon devices for inner vertex detectors.

Exhibit A

Director's Office
Laboratory Directed Research and Development Program

BROOKHAVEN
NATIONAL LABORATORY

Building 815E
P.O. Box 5000
Upton, NY 11973-5000
Phone 631 344-4467
Fax 631 344-2887
newman@bnl.gov

managed by Brookhaven Science Associates
for the U.S. Department of Energy

Memo

date: *January 2, 2001*

to: *Distribution*

from: *L. Newman L.N.*

subject: *Laboratory Directed Research & Development Program (LDRD) Proposals*

This is to solicit proposals for the annual LDRD competition. The LDRD schedule is shown below. Proposals must be submitted by April 2, 2001, through the respective Chairperson and Associate Laboratory Director to BNL's Administrator for LDRD (Kevin Fox in Bldg. 460), using the attached submission forms (electronic versions can be obtained from greco@bnl.gov). **Please note that we are now requiring a proposal, but not more than three pages in length, in addition to the previously requested abstract.**

Research conducted under LDRD should be highly innovative and an element of high risk as to success is acceptable. **We would like to especially encourage "emerging" scientists to submit proposals.** To help individuals with the preparation of viable proposals, the BNL LDRD Policy, which defines the LDRD program, can be reviewed at https://sbms.bnl.gov/ld/ld03/ld03d011.htm. In my capacity as Scientific Director for LDRD, I am available to counsel individuals to aid them in their preparation of a successful proposal.

Please note that LDRD projects are restricted to a maximum of three years. However, projects should be tailored to a two-year schedule, and the following information should be incorporated into all proposals.

***New projects*:** New proposals must include a milestone schedule of activities to be completed by the mid-year, 1st year, 2nd year, and 3rd year reviews (see attached schedule). Include in the schedule planned accomplishments and dates of completion (i.e. completed lab setups, run tests or trials, compiled data, issued reports on results, etc).

The Evaluation Committee will, as in the past, be chaired by the Deputy Director for Science and Technology and consist of the Associate Laboratory Directors augmented by selected distinguished scientists. The committee starts meeting in April to evaluate proposals for FY 2002 funding.

For planning purposes, the following is the calendar for LDRD activities:

January 2, 2001	Call for FY 2002 Proposals
March 19-23, 2001	FY 2001 Mid-Year Review
April 2, 2001	FY 2002 Proposals Due
May 15, 2001	Selection of FY 2002 LDRDs
August 15, 2001	FY 2002 Plan Due to DOE
September 14, 2001	Call for FY 2001 Annual Reports
October 1, 2001	Funding of FY 2002 Projects
October 15, 2001	Annual Reports Due on FY 2001 Projects
December 31, 2001	Draft FY 2001 Annual Report to DOE - BHG
March 31, 2002	FY 2001 Annual Report Due to DOE

LN:kjf
Attachments

Distribution:
Associate Laboratory Directors
Department Chairpersons

cc: F. Federmann
G. Fess
K. Fox
W. Hempfling
J. Marburger
N. Narain
P. Paul
Assistant Laboratory Directors
Division Managers

Exhibit B

Director's Office
Laboratory Directed Research and Development Program

BROOKHAVEN NATIONAL LABORATORY

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Upton, NY 11973-5000
Phone 631 344-4467
Fax 631 344-2887
newman@bnl.gov

managed by Brookhaven Science Associates
for the U.S. Department of Energy

Memo

date: *April 11, 2001*

to: *Distribution*

from: *L. Newman L.N.*

subject: *FY 2002 LDRD Proposals for Review*

We are about to enter the important process of selecting LDRD projects for support in the next fiscal year. We have received 81 proposals in good order, and they are listed in the enclosed table. I am establishing a process this year that will expedite the selection process and hopefully result in the selection of the most noteworthy projects for funding.

The ALD, as the most qualified expert, will serve as the first proponent for all proposals in their area. We have already indicated in the table where we believe you are the first proponent (1P). If we have made any mistakes now is the time to let us know. In addition, the ALDs will serve as a second proponent for one third of the remaining proposals. The two scientists from the Brookhaven Council will be assigned to one half of the proposals for which they will serve as second proponents.

In order to assign you the proposals that you will feel most comfortable with reviewing, I propose that on the enclosed table you select proposals, based on the title, by marking those that you are highly interested in (H), moderately interested in (M), or have no interest in (N); and if I receive the information by **April 19,** I will try to comply with your wishes in the assignment process. Eventually you will be receiving copies of all the proposals and are encouraged to familiarize yourself with them prior to the our meeting.

You will be expected to come to the first meeting having already decided on tentative rankings for all proposals for which you are the first or second proponent and provide this information at the onset of the meeting. We will then have a discussion of each of the proposals led by the principal proponent with augmentation by the two second proponents, upon which we will all be asked to provide our rankings. Dr. Paul and I will have read all proposals prior to the meeting but will not provide their rakings until after the discussion. We will be using a ranking process consisting of: highest priority (4), high priority (3), fund if possible (2), or low priority (1). Please remember while making your rankings that we will only be able to fund a small fraction of the proposals and that we are committed to select meritorious activities from "emerging scientists."

LN/dj
attachment
Distribution:
ALDs
K. Fox
J. Gatley
S. Hulbert
P. Paul
C. Wirick

Exhibit C

The only official copy of this file is the one on-line in SBMS. Before using a printed copy, verify that it is the most current version by checking the document issue date on the BNL SBMS website.

Issue Date: March 1999

Point of Contact: Laboratory Directed Research and Development Subject Matter Expert

Laboratory Directed Research and Development (LDRD) Program

I. Purpose

To encourage and support the development of new ideas that could lead to new programs, projects, and directions, the Laboratory will fund exploratory work by members of its staff.

II. General

The LDRD program focuses on early exploration and exploitation of creative and innovative concepts, which enhance the ability of the Laboratory to carry out its current and future mission objectives in line with the goals of the Department of Energy. This discretionary research and development tool is viewed as one important way of maintaining the scientific excellence of the Laboratory. It is a means to stimulate the scientific-technological community (foster new science and technology ideas), which is a factor in achieving and maintaining staff excellence, and is a means to address national needs within the overall mission of the DOE.

III. General Characteristics of the LDRD Program

Projects or studies that are appropriate candidates for the Laboratory Directed Research and Development Program (LDRD) are normally small, ranging from $50,000 to $200,000 per year, with a preference for smaller projects. They are generally funded for periods of two years with a

possible continuation for a third year. Typically they include but are not limited to:

- Projects in the forefront areas of basic and applied science and technology for the primary purpose of enriching laboratory capabilities.
- Advanced study of new hypotheses, new concepts, or innovative approaches to scientific or technical problems.
- Experiments and analyses directed toward "proof of principle" or early determination of the utility of new scientific ideas.
- Conceptual and preliminary technical analysis of experimental facilities or devices.

IV. Procedures

Proposal preparation, submission, review and approval:

- Proposals for the following fiscal year will be solicited by January 1 for submission by April 1. Awards will be made by May 1 on a competitive basis. Normally LDRD projects will start shortly after the beginning of the fiscal year.
- Applications should consist of an abstract and a three page proposal outlining the planned project. Applicants are encouraged to be brief but to provide sufficient information on the purpose of the project and the method of accomplishment. A copy of the Proposal Information Questionnaire **must** also be completed by the initiator and approved by the appropriate Department Administrator, Department Chairperson or Division Head. Completed applications are submitted to the Department Chairperson who forwards it to the Scientific Director for LDRD who acts as the Chairperson of the LDRD Selection Committee.
- The LDRD Committee consists of the Deputy Director, the LDRD Scientific Director, all Associate Laboratory Directors, and two senior scientists chosen from the Brookhaven Council. The Committee reviews all proposals, obtains additional information deemed necessary, and selects the projects to be funded and the amount of each award.
- When an LDRD research project is authorized for funding, the principal investigator will be notified, as well as the cognizant Department Chairperson or Division Head. The Assistant Budget Office will establish a separate Laboratory overhead account to budget and collect the costs for the project.
- The total amount of funds to be made available for the program, and accordingly the number of projects supported, will vary from year to year, dependent to a large extent on the Laboratory's overall financial situation, and on the amount approved by DOE.

Reporting Requirements:

- In March of each year, the full LDRD Committee shall perform a formal mid-year review of all LDRD projects. This review will ascertain the progress and quality of the research performed.

- After the start of the project, interim annual status reports are required for each project and must be submitted by November 1 to the LDRD Scientific Director. These status reports should provide a brief summary (outlining purpose, approach, and status or progress of two pages or less) of the results of the LDRD project. Projects of more than one year should only summarize progress since the previous report. Additionally, the status report should also identify significant findings or accomplishments, papers, publications, patents, follow-on funding (includes funds requested or approved from other), support of post-docs or other students, presentations, and copyrights. For multi-year projects the goals for the following years should be updated in view of the previous year's experience.

- A written final report is required to be submitted within thirty days after the end of the project to the LDRD Scientific Director. The report should provide a summary of the results of the LDRD project as well as identify the significant findings, all papers, publications, patents, proposals, support of post-docs or other students, presentations, and copyrights that result from the study. If a proposal for new agency-funded research has been prepared, a copy should be enclosed with the report. If a proposal will be prepared, identify the funding agency and specific program and send a copy to the LDRD Scientific Director when it is submitted to the funding agency.

V. Restrictions

The purpose of the program is to develop new, fundable programs at Brookhaven. As such, the work proposed should be consistent with the missions of the Laboratory and the DOE and NRC. In this regard, the Laboratory's Institutional Plan and Agency program documents serve as guidance.

- Awards will not be made to substitute for, or increase funding for any tasks for which Congress or the DOE has established a specific limitation or for any specific tasks that are funded by DOE or other users of the laboratory.

- The exploratory study should not require the acquisition of permanent staff.

- It is expected that projects will be modest in size and limited to 3 years or less.

- The award will not fund activities that will require the addition of non-LDRD funds in order to reach a useful stage of completion.

- The LDRD study will not

1. fund construction line-item projects, in whole or in part,
2. fund construction design beyond the preliminary phase (e.g. conceptual design, Title I design work, or any similar or more advanced effort may not be supported),
3. Fund capital equipment expenditures. Any preliminary design work before conceptual design which is supported, must be directly associated with an LDRD project.

Exhibit D

BROOKHAVEN NATIONAL LABORATORY
PROPOSAL INFORMATION QUESTIONNAIRE
LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

PRINCIPAL INVESTIGATOR _____ PHONE _____

DEPARTMENT/DIVISION _____ DATE _____

OTHER INVESTIGATORS _____

TITLE OF PROPOSAL _____

PROPOSAL TERM
From (month/year) _____ To (month/year) _____

SUMMARY OF PROPOSAL Provide an abstract of the proposed project which clearly defines the central idea of the project scope, its purpose and what it hopes to accomplish. Also indicate how it meets the general characteristics of the LDRD Program. This should not exceed the space given below. Attach an extended proposal of no more then three (3) pages in length plus a milestone schedule.

Proposal

LDRD Milestone Schedule	
Date	Planned Accomplishments
Six Months	
1 year	
18 months	
2 years	
30 months	
3 years	

HUMAN SUBJECTS (Reference: DOE Order 1300.3)

Are human subjects involved from BNL or a collaborating institution?

If YES, attach copy of the current Institutional Review Board Approval and Informed Consent Form from BNL and/or collaborating institution. Y/N _____

VERTEBRATE ANIMALS

Are vertebrate animals involved? Y/N _____

If yes, has approval from BNL's Animal Care and Use Committee been obtained? Y/N _____

NEPA REVIEW

Are the activities proposed similar to those now carried out in the department/division which have been previously reviewed for potential environmental impacts and compliance with federal, state, local rules and regulations, and BNL's Environment, Safety, and Health Standards. (Therefore, if funded, proposed activities would require no additional environmental evaluation.) Y/N _____

If no, has a NEPA review been completed in accordance with the Subject Area National Environmental Policy Act (NEPA) and Cultural Resources Evaluation and the results documented? Y/N _____

(Note: if a NEPA review has not been completed, submit a copy of the work proposal to the BNL NEPA Coordinator for review. No work may commence until the review is completed and documented.)

ES&H CONSIDERATIONS

Does the proposal provide sufficient funding for appropriate decommissioning of the research space when the experiment is complete? Y/N _____

Is there an available waste disposal path for project wastes throughout the course of the experiment? Y/N _____

Is funding available to properly dispose of project wastes throughout the course of the experiment? Y/N _____

Can the proposed work be carried out within the existing safety envelope of the facility (Facility Use Agreement, Nuclear Facility Authorization Agreement, Accelerator Safety Envelope [ASE], etc.) in which it will be performed? Y/N _____

If not, what has to be done to prepare the facility to accept the work (modify the facility, revise the SAR/SAD, revise the Facility Use Agreement, etc.)and how will the modifications be funded? Y/N _____

FUNDING REQUESTED [ATTACH A DETAILED BUDGET BREAKDOWN]

[Break down the funding by fiscal year and by the broad categories of labor, materials and supplies, travel (foreign & domestic), services and subcontracts. LDRD funds cannot be used to purchase capital equipment. Indicate the intent to use collaborators and/or postdoctoral students, if applicable. Identify the various burdens applied, i.e., materials, organizational contracts. The Laboratory G&A should not be applied.]

POTENTIAL FUTURE FUNDING

Identify below the Agencies and the specific program/office which may be interested in supplying future funding. Give some indication of time frame.

Approvals

Department /Division Administrator _____

Department/Division Head _____

Cognizant Associate Director _____

BUDGET REQUEST BY FISCAL YEAR
(Note: Funding cannot exceed 3 years)

COST ELEMENT	FISCAL YEAR _____	FISCAL YEAR _____	FISCAL YEAR _____
Labor * Fringe Total Labor Organizational Burden @ ____ %			
Materials Supplies Travel Services Total MST Materials Burden @ ____%			
Sub-contracts Contracts Burden @ ____%			
Electric Power CCD Charge Other (specify)			
TOTAL PROJECT COST			
* Labor (indicate type of staff and level of effort)			
List all materials costing over $5000.			