

Brookhaven National Laboratory's
Annual Report of
Laboratory Directed
Research & Development
Program Activities
For FY 2003

Director's Office

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
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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 413.2A, "Laboratory Directed Research and Development," January 8, 2001, 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 413.2A.

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 2003. 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 2003 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 2004. The BNL LDRD budget authority by DOE in FY 2003 was \$8.5 million. The actual allocation totaled \$7.8 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 (ALDF) 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 2003, the Program Committee--which selected the 2004 programs--consisted of eight members. The Scientific Director of the LDRD Program chaired the Committee, and the other members were the Deputy Director for Science & Technology (DDS&T), four Associate Laboratory Directors (ALDs), and four members from the scientific departments and divisions.

2003 LDRD PROGRAM COMMITTEE

| | |
|-----------------------|---|
| Leonard Newman | Chairperson (SD) |
| Peter Paul | Deputy Director for Science & Technology (DDS&T) |

| | |
|--------------------------|--|
| Ralph James | Energy, Environment & National Security (ALD) |
| Thomas Kirk | High Energy & Nuclear Physics (ALD) |
| Helene Benveniste | Life Sciences (Interim ALD) |
| Doon Gibbs | Basic Energy Sciences (Interim ALD) |
| Morris Bullock | Chemistry (S) |
| James Davenport | Data Intensive Computing (S) |
| Joseph Brennan | Collider Accelerator (S) |
| Paul Freimuth | Biology (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 DDS&T for LDRD and in consultation with the ALDF, 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 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, the LDRD budget has been increased over the past ten years from \$2.0 million to \$9.5 million, or from less than 1% to almost 2% of the laboratory budget. The target level is to go to about 4%, which would still be significantly less than the DOE mandated maximum of 6%.

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 letter is sent by the SD for LDRD to the Scientific Staff and as a separate memorandum to all the Associate Laboratory Directors and Department Chairpersons. The FY 2004 call issued in February 2003 is attached as Exhibit A. This early schedule better facilitated the recruitment of post-doctorate candidates to support LDRD projects. We continued the process initiated in FY 02 that permits the deferral of expending the budget allocation into a third year to permit the full funding of post doctorates for two years, as they might not arrive at the onset of the LDRD project. The call references the BNL LDRD Standards-Based Management System (SBMS) Subject Area, which is available to

all employees on the web at <https://sbms.bnl.gov/standard/3c/3c00t011.htm>. The other method is through a feature article in The Bulletin, the Laboratory's weekly newspaper.

The LDRD SBMS Subject Area 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 B. 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 computational biology. Then these "areas of interest" are communicated broadly to the scientific staff

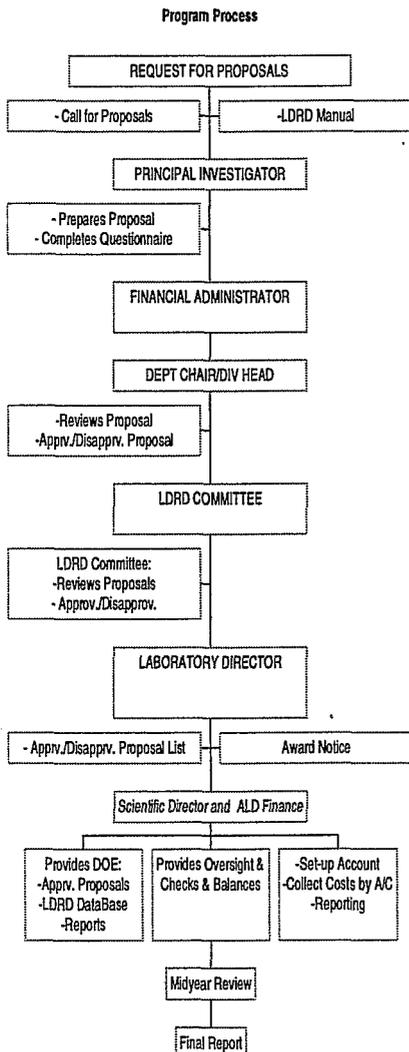
and in particular to staff members who are known to be in a position to pursue and develop their ideas in the form of a more formal proposal.

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 the abstracts 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. One other ALD and a S serve as second proponents. The SD serves as a third proponent for all of the proposals. All of the above receive for review the full proposals for which they are responsible. A description of the process is outlined in the Figure above. All members have several weeks to review the proposals and prepare for a full debate on each proposal.

Selection Criteria: Minimum requirements for 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 generally 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 SBMS Subject Area 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 413.2A are also



carefully considered during the selection process to ensure that proposals are consistent with DOE criteria.

Project Approval: After all proposals are discussed, the Committee selects the highest priority proposals by concurrence. 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 approval. After approval by the Director all new projects are submitted to the DOE-Brookhaven Area Office (DOE-BAO) for concurrence prior to start. The ALDF 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 monitors the project's status, schedule, and progress and coordinates with the chairperson or manager as necessary.

The SD 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, the DDS&T, the cognizant ALD and Department Chair, and a representative from the ALDF and DOE-BAO. This review checks on the progress of the projects including its funding schedule. This allows the SD to ensure that the work is being completed in a timely manner.

In addition, the SD conducts a monthly meeting with the DOE LDRD Project Manager 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-BAO 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.). We now have a Data Collection Form (Exhibit C) so that we can more formally collect information on the

impacts of the projects. Each project will be tracked for two years after its completion so as to gather a complete set of information on the impact of the project. Also, we input LDRD data into the DOE-Chief Financial Officer's Laboratory/Plant Directed Research and Development Web Site (<https://ldrd.rpt.doe.gov/>) to support DOE reporting of LDRD to Congress.

Some of the projects may involve animals or humans. Those projects will 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 that includes the Deputy Director for Science and Technology and the cognizant Department Chair and Associate Laboratory Director.

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 Laboratory. In FY 2003, BNL updated last year's 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 most recent 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.

The FY 2004 LDRD Plan was submitted to DOE in August of 2003 for review. In October of 2003 the 2004 Plan was approved, and DOE-HQ informed the DOE-BAO that the plan was an excellent document.

The FY 2002 favorable customer satisfaction was a result of the SD of the LDRD and ALDF 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. Increase awareness of the LDRD Program to the Laboratory scientific community by publishing articles in Brookhaven Bulletin and Monday Morning Memo. Also conducting presentations to the Science Council and Science and Technology Steering Committee
2. Better communicate and integrate Laboratory Strategic Plan with the LDRD Program by supporting the new Integrated Planning Office in integration of LDRD program with the Laboratories overall Strategic Plan.
3. Review the existing selection process for possible changes.
4. Conduct a customer survey in FY 2004
5. Consider utilizing a 3rd party peer review

The self assessments contain meaningful recommendations and will continue to 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 elements in its mission which support the four DOE programmatic business lines.

SCIENCE & 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 PROGRAMS

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

ENERGY RESOURCE MISSION, ENERGY TECHNOLOGIES

Perform R&D to provide clean, sustainable energy focusing on basic and applied research, system analysis and technology development.

NATIONAL SECURITY MISSION

Focus on domestic and international programs in nonproliferation and national security.

ENVIRONMENTAL QUALITY MISSION

Remediate the site and decontaminate and decommission of several research reactors.

TECHNOLOGY TRANSFER

Developing, managing, and transferring to industry intellectual property and technical know-how associated with research discoveries.

The 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 Tables 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
- Porphyrin chemistry

- Electrochemistry

Environmental Sciences:

- Global change
- Atmospheric chemistry
- Marine science
- Soil chemistry
- Cycling of pollutants
- Environmental remediation
- Counter Terrorism

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 <ul style="list-style-type: none"> • RHIC • NSLS • ATF • LEAF • STEM • Tandem • BMRR | 0 |
| 2 | Nuclear Physics <ul style="list-style-type: none"> • Quark/gluon plasma • Spin Physics | 0 |
| 3 | High Energy Physics <ul style="list-style-type: none"> • Standard Model • Rare Particles & Processes | 1 |
| 4 | Advanced Accelerator & Detector Concept and Designs - Advanced Instrumentation <ul style="list-style-type: none"> • Muon Collider • DUV-FEL • LHC • SNS | 14 |
| 5 | The Physics & Chemistry of Materials <ul style="list-style-type: none"> • Superconductivity • Magnetism • Surfaces • Nanostructure | 21 |
| 6 | Energy Sciences <ul style="list-style-type: none"> • Combustion • Catalysis • Bio-fuels • Batteries • Geothermal • Buildings | 13 |
| 7 | Environmental Sciences <ul style="list-style-type: none"> • Atmospheric • Terrestrial • Bio-remedial • Waste Technologies • Counter Terrorism | 14 |
| 8 | Medical and Imaging Sciences & Technology | 5 |
| 9 | Advanced Computation | 0 |
| 10 | Biological Sciences | 14 |
| 11 | Critical Infrastructure | 1 |
| Totals | | 83 |

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 productivity of the LDRD Program.

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. Essentially all of the scientific departments were represented in the FY 2003 LDRD Program. The LDRD Program at BNL is expanding and is generating interest from across the entire Laboratory population.

In FY 2003, the BNL LDRD Program funded 83 projects, 44 of which were new starts, at a total cost of \$7,830,078. Included in this report is the Project Funding Table, which lists all of the FY 2003 funded projects and gives a history of funding for each by year.

| FY | DOE Authorized K\$ | BNL AUTH K\$ | COSTED K\$ | NO. REC'D | NEW STARTS |
|--------|--------------------|--------------|------------|-----------|------------|
| 1985 | 4,000 | 1,842 | 1,819 | 39 | 13 |
| 1986 | 4,500 | 2,552 | 2,515 | 22 | 15 |
| 1987 | 4,000 | 1,451 | 1,443 | 29 | 8 |
| 1988 | 4,000 | 1,545 | 1,510 | 46 | 14 |
| 1989 | 4,000 | 2,676 | 2,666 | 42 | 21 |
| 1990 | 4,000 | 2,008 | 1,941 | 47 | 9 |
| 1991 | 2,000 | 1,353 | 1,321 | 23 | 14 |
| 1992 | 2,500 | 1,892 | 1,865 | 30 | 14 |
| 1993 | 2,500 | 2,073 | 2,006 | 35 | 14 |
| 1994 | 2,500 | 2,334 | 2,323 | 44 | 15 |
| 1995 | 2,500 | 2,486 | 2,478 | 46 | 13 |
| 1996 | 3,500 | 3,500 | 3,050 | 47 | 17 |
| 1997 | 4,500 | 4,500 | 3,459 | 71 | 10 |
| 1998 | 3,500 | 4,000 | 2,564 | 53 | 4 |
| 1999 | 4,750 | 4,612 | 4,526 | 67 | 25 |
| 2000 | 6,000 | 6,000 | 5,534 | 93 | 21 |
| 2001 | 6,000 | 6,000 | 5,345 | 97 | 38 |
| 2002 | 7,000 | 7,000 | 6,732 | 87 | 29 |
| 2003 | 8,500 | 8,482 | 7,830 | 153 | 44 |
| 2004 | 9,500 | 8,550 | | 107 | 20 |
| TOTALS | 89,750 | 74,078 | 60,975 | 1,178 | 358 |

An analysis of the FY 2003 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. A summary of success indicators for the FY 2003 projects is as follows:

| SUCCESS INDICATORS | QTY |
|--|-----|
| Total number of refereed publications based on the work supported by LDRD funds and done during the active period of this project. | 148 |
| Total number of formal presentations originating in whole or in part from this LDRD, including those that have been accepted for presentation but not yet presented. | 255 |
| Total number of reports originating in whole or in part from this LDRD. | 15 |
| Total number of patent and licenses either applied for or granted that were either derived from this LDRD project directly or from any follow-on efforts to date. | 5 |
| Total number of copyrights either applied for or granted that were either derived from this LDRD project directly or 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. | 5 |
| Total number of review presentations that pertain to this work. | 12 |
| Total number of students and postdocs (combined total as FTEs) directly supported by this LDRD project while this project was active. | 87 |
| Total number of new, permanent, full-time staff hired as a direct result of this LDRD Project. | 26 |
| Total number of proposals submitted for follow-on funding (other than LDRD). | 73 |
| Total number of national awards or recognitions received that are attributable in whole or in part from this LDRD. | 5 |

In conclusion, the overall LDRD Program has been successful. In FY 2003, the LDRD Program has improved on the level established in FY 2002 which already was at a high level. 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 2003 the Laboratory continued to experience a significant scientific gain by the achievements of the LDRD Projects.

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

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2003

| | | | | | Actual | Actual | Actual | Approved Budget | Requested Budget | Total |
|----------------|---|-----------------|-------------|-------|-----------|-----------|-----------|-----------------|------------------|-------------|
| LDRD Proj. No. | Project Title | P.I. | Dept./Bldg. | Theme | FY 01\$ | FY 02\$ | FY 03 \$ | FY 04 \$ | FY 05 \$ | |
| 01-13 | "Functional Spectral Signature" (FSS) Method for Signal to Noise-Enhancement of Brain Patterns in PET Images | Felder, C. | MED/490 | 10 | \$85,941 | \$45,085 | \$41,383 | | | \$172,409 |
| 01-30 | Development of CZT Array Detector Technology for Synchrotron Radiation Applications | Siddons, D. P. | NSLS/725D | 4 | \$106,592 | \$68,399 | \$50,418 | | | \$225,409 |
| 01-31 | New Applications of Circular Polarized VUV-light (NANO IV) | Vescovo, E. | NSLS/725D | 5 | \$23,860 | \$52,904 | \$51,191 | | | \$127,955 |
| 01-35 | Prototype Approaches Toward Infrared Nanospectroscopy | Carr, G. L. | NSLS/725D | 5 | \$33,689 | \$64,030 | \$43,818 | | | \$141,537 |
| 01-36 | Pressure-Induced Protein Folding Monitored by Small Angle X-Ray Scattering and Fourier Transform Infrared Microspectroscopy | Miller, Lisa | NSLS/725D | 10 | \$43,499 | \$43,511 | \$49,620 | | | \$136,630 |
| 01-38 | Soft Condensed Matter Probed by Low-Energy Resonant Scattering | Caliebe, W. | NSLS/725D | 5 | \$32,873 | \$50,401 | \$49,422 | | | \$132,696 |
| 01-39 | Femto-Seconds Electron Microscope Based on the Photocathode RF Gun | Wang, X. J. | NSLS/725C | 4 | \$145,593 | \$62,119 | \$64,622 | | | \$272,334 |
| 01-51 | Human DNA Damage Responses: DNA-PK and p53 | Anderson, C. W. | BIO/463 | 10 | \$167,158 | \$124,613 | \$61,706 | | | \$353,477 |
| 01-87 | Charge Transfer on the Nano Scale: Theory (NANO III) | Newton, M. D. | CHEM/555A | 5 | \$43,063 | \$54,429 | \$17,512 | | | \$115,004 |
| 01-93 | High Resolution Magneto-optical Study of Magnetic Nanostructures, Nanocomposite Functional and Superconducting Materials (NANO IV) | Li, Qiang | MSD/480 | 5 | \$32,748 | \$45,797 | \$26,000 | | | \$104,545 |
| 02-02 | Crystallization and X-ray Analysis of Membrane Proteins | Fu, D. | BIO/463 | 10 | | \$380,454 | \$396,551 | \$414,400 | | \$1,191,405 |
| 02-03 | <i>In Vitro</i> Investigation of the DNA Double Strand Break Repair Mechanism by Non-Homologous End-Joining in the context of Chromatin | Lymar, E. | BIO/463 | 10 | | \$63,659 | \$61,070 | | | \$124,729 |
| 02-08 | Creating a MicroMRI Facility for Research and Development | Benveniste, H. | MED/490 | 4 | | \$94,494 | \$193,613 | \$180,000 | | \$468,107 |
| 02-09 | Targeting Tin-117m to Estrogen Receptors for Breast Cancer Therapy | Kolsky, K. | MED/801 | 10 | | \$48,242 | \$98,671 | \$50,000 | | \$196,913 |
| 02-16 | Biominaleralization of Actinides: A Mechanistic Study of the Genesis of Novel and Stable Compounds | Francis, A. J. | ESD/490A | 7 | | \$88,871 | \$92,482 | | | \$181,353 |
| 02-17 | Using Mini-LIDAR for Verification and Long-Term Monitoring of Cover Systems | Heiser, J. | ESD/830 | 6 | | \$124,610 | \$124,084 | | | \$248,694 |

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2003

| | | | | | Actual | Actual | Actual | Approved Budget | Requested Budget | Total |
|----------------|---|------------------|-------------|-------|---------|-----------|-----------|-----------------|------------------|-----------|
| LDRD Proj. No. | Project Title | P.I. | Dept./Bldg. | Theme | FY 01\$ | FY 02\$ | FY 03 \$ | FY 04 \$ | FY 05 \$ | |
| 02-22 | Electrical Systems Reliability | Bari, R. | ES&T/475B | 11 | | \$83,965 | \$99,081 | \$104,000 | | \$287,046 |
| 02-24 | Liquid Fuel Gasifier for Combustion and Fuel Cells | Butcher, T. | ES&T/526 | 6 | | \$72,993 | \$107,892 | | | \$180,885 |
| 02-31 | Study of a Power Source for Nano-Devices | Lin, M. | ES&T/815 | 5 | | \$99,920 | \$99,045 | | | \$198,965 |
| 02-42 | Ultrafast Nonlinear Spectroscopic Studies of Model Catalytic Surfaces | Camillone, N. | CHEM/555 | 6 | | \$184,847 | \$185,275 | | | \$370,122 |
| 02-45 | Combined Use of Radiotracers and Positron Emission Imaging in Understanding the Integrated Response of Plants to Environmental Stress | Ferrieri, R. | CHEM/901 | 7 | | \$99,220 | \$99,809 | \$150,000 | | \$349,029 |
| 02-46 | Arranging Nanoparticles into Arbitrary Patterns with Optical Trapping | Fockenber, C. | CHEM/555A | 5 | | \$119,860 | \$119,807 | | | \$239,667 |
| 02-48 | Advanced Multidimensional Techniques to Explore the Biochemical and Behavioral Consequences of VOC Exposure | Gerasimov, M. R. | CHEM/555A | 7 | | \$119,827 | \$94,788 | | | \$214,615 |
| 02-49 | Project to Detect pp and 7Be Solar Neutrinos in Real Time: LENS, the Low-Energy Neutrino Spectrometer | Hahn, R. | CHEM/555A | 3 | | \$70,248 | \$70,006 | | | \$140,254 |
| 02-53 | Combined Theoretical and Experimental Study of Crystal Lattice Defects in Complex Transition Metal Oxides | Davenport, J. | DA/463B | 5 | | \$39,678 | \$65,745 | | | \$105,423 |
| 02-55 | Chemical Sensors: Immobilization of Organometallic Complexes into Sol-gel Matrices | Renner, M. | MSD/555 | 6 | | \$81,940 | \$84,607 | | | \$166,547 |
| 02-56 | Size Dependence of Catalytic Reactivity of Iron Oxide Nanocrystals | Wong, S. | MSD/480 | 6 | | \$84,575 | \$104,354 | | | \$188,929 |
| 02-58 | Femtosecond Synchronization for Ultra-Short Pulse DUV-FEL Radiation | Graves, W. | NSLS/725D | 4 | | \$134,883 | \$134,776 | | | \$269,659 |
| 02-62 | Rapid Wavelength Tunability for the DUV-FEL | Sheehy, B. | NSLS/725D | 4 | | \$135,269 | \$135,269 | | | \$270,538 |
| 02-66 | High-Gain Harmonic-Generation at the DUV/FEL | Yu, L. H. | NSLS/725C | 4 | | \$134,947 | \$134,612 | | | \$269,559 |
| 02-67 | Biominaleralization: A Route to Advanced Materials | DiMasi, E. | CMP/510B | 5 | | \$99,935 | \$103,076 | | | \$203,011 |
| 02-70 | Theory of Electronic Transport in Nanostructures and Low-Dimensional Systems | Tselik, A. | CMP/510A | 5 | | \$134,268 | \$110,055 | \$145,500 | | \$389,823 |
| 02-71 | Pressure in Nanopores | Vogt, T. | CMP/510B | 5 | | \$79,000 | \$72,856 | \$54,900 | | \$206,756 |

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2003

| | | | | | Actual | Actual | Actual | Approved Budget | Requested Budget | Total |
|----------------|--|-------------------|-------------|-------|---------|-----------|-----------|-----------------|------------------|-----------|
| LDRD Proj. No. | Project Title | P.I. | Dept./Bldg. | Theme | FY 01\$ | FY 02\$ | FY 03 \$ | FY 04 \$ | FY 05 \$ | |
| 02-84a | Genomic SELEX to study Protein DNA/RNA Interactions in <i>Ralstonia Metallidurans</i> CH34 Regulating Heavy Metal Homeostasis and Resistance | van der Lelie, D. | BIO/463 | 10 | | \$163,972 | \$167,824 | \$165,000 | | \$496,796 |
| 02-84b | Lead Resistance in <i>Ralstonia Metallidurans</i> CH34 | van der Lelie, D. | BIO/463 | 10 | | \$161,408 | \$168,766 | \$170,000 | | \$500,174 |
| 02-85 | Design of a <i>Ralstonia Metallidurans</i> Two-Hybrid Protein System for Studying Signaling Pathways Regulating Heavy Metal Homeostasis and Resistance | Taghavi, S. | BIO/463 | 10 | | \$168,188 | \$172,175 | | | \$340,363 |
| 02-86 | Ultrafast X-Ray Science | Dierker, S. | NSLS/725B | 5 | | \$100,018 | \$107,670 | \$105,000 | \$50,000 | \$362,688 |
| 02-88 | X-Ray Photon Correlation Spectroscopy Studies of Nanostructured Block Copolymers | Dierker, S. | NSLS/725B | 5 | | \$90,212 | \$104,806 | \$105,000 | \$50,000 | \$350,018 |
| 02-91 | Fine Grain Gas and Silicon Detectors for Future Experiments in Nuclear Physics at High Energies | Woody, C. | PHYS/510C | 4 | | \$99,511 | \$96,559 | | | \$196,070 |
| 03-004 | High-Brightness, High-Power Electron Beams | Ben-Zvi, I. | CAD/725C | 4 | | | \$149,624 | \$192,000 | \$190,000 | \$531,624 |
| 03-006 | Feasibility Study of Optical Stochastic Cooling with a CO2 Laser | Yakimenko, V. | PHY/820M | 4 | | | \$109,205 | \$126,400 | \$130,000 | \$365,605 |
| 03-013 | Proposal for Niobium/Tin Superconducting Magnet | Willen, E. | SMD/902A | 4 | | | \$147,824 | \$157,300 | | \$305,124 |
| 03-014 | Technology Development for Linear Collider Final Focus Quadrupoles with Small-Aperture High-Gradient Superconducting Coils | Parker, B. | SMD/902A | 4 | | | \$124,829 | \$130,000 | | \$254,829 |
| 03-025 | Real-Time Detection and Multi-Dimensional Characterization of Single Air-Borne Microorganism | Zelenyuk, A. | ESD/815E | 7 | | | \$99,570 | | | \$99,570 |
| 03-026 | Developing a New, Unified Systems Theory on Size Distributions of Atmospheric Particles | Liu, Y. | ESD/815E | 7 | | | \$45,495 | \$45,637 | | \$91,132 |
| 03-027 | Measurement of HO2 Radicals by ChemiLuminescence Analysis of Atmospheric Radicals (CLAAR) | Springston, S. | ESD/815E | 7 | | | \$99,480 | \$100,000 | | \$199,480 |
| 03-030 | Chemistry of the Rhizosphere | Fuhrmann, M. | ESD/830 | 10 | | | \$99,360 | \$102,157 | | \$201,517 |
| 03-039 | Integrated Analysis of Carbon and Nitrogen Metabolism in Plants and Subsequent Analysis of Photosynthetic Acclimation to Growth in Elevated pCO2 | Rogers, A. | ESD/490D | 7 | | | \$65,782 | \$67,924 | | \$133,706 |
| 03-050 | Evaluation of High-Energy Radiation Effects in Materials | Finrock, C. | ES&T/703 | 5 | | | \$98,424 | \$106,000 | | \$204,424 |
| 03-056 | Structural Properties of Methane Hydrates | Mahajan, D. | ES&T/815 | 6 | | | \$83,870 | \$104,000 | \$15,000 | \$202,870 |

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2003

| | | | | | Actual | Actual | Actual | Approved Budget | Requested Budget | Total |
|----------------|--|-------------------------------|-------------|-------|---------|---------|-----------|-----------------|------------------|-----------|
| LDRD Proj. No. | Project Title | P.I. | Dept./Bldg. | Theme | FY 01\$ | FY 02\$ | FY 03 \$ | FY 04 \$ | FY 05 \$ | |
| 03-061 | Dynamics of Wind Turbine-Tower-Foundation Systems | Philippacopoulos, A. | ES&T/526 | 6 | | | \$138,302 | \$146,000 | | \$284,302 |
| 03-064 | Investigation of Neutron and Gamma Probes to Detect Explosives in Sealed Containers | Todosow, M. | ES&T/475B | 7 | | | \$108,782 | \$115,000 | \$120,000 | \$343,782 |
| 03-065 | Ultrasound and Infrared Imaging to Detect Degradation of Electric Cable Insulation | Villaran, M. | ES&T/130 | 6 | | | \$61,439 | \$75,000 | | \$136,439 |
| 03-072 | Application of Compton-Suppression Gamma Spectrometry to Problems in Anti-Terrorism | Lemley, J. | NNS/197C | 7 | | | \$122,783 | \$128,000 | | \$250,783 |
| 03-077 | Real-Time Consequence Assessment System for Atmospheric Terrorist Events in the Northeast Urban Corridor | Reynolds, R.M. for Hansen, D. | ESD/490D | 7 | | | \$69,765 | \$73,000 | | \$142,765 |
| 03-081 | Application of Thin Film-Like Dosimeters for Port Security and Anti-Terrorism | Kaplan, E. | NNS/197D | 7 | | | \$109,079 | \$113,000 | | \$222,079 |
| 03-083 | Novel Xenon Detector Concepts for Homeland Defense | Vanier, P. | NNS/197C | 7 | | | \$99,029 | \$104,000 | | \$203,029 |
| 03-086 | Defining New Pathways for Disarming Anthrax Toxin | Freimuth, P. | BIO/463 | 7 | | | \$99,955 | \$100,000 | | \$199,955 |
| 03-094 | Structural Studies on the Integral Membrane Protein AlkB | Shanklin, J. | BIO/463 | 10 | | | \$52,754 | \$98,000 | \$40,000 | \$190,754 |
| 03-098 | Roles of Dopamine Receptor Agonists in Brain Metastasis of Breast Cancer | Lin, X. | MED/490 | 8 | | | \$97,812 | \$100,000 | \$150,000 | \$347,812 |
| 03-099 | The microPET Study of Gene Expression in Rodents | Thanos, P. | MED/490 | 8 | | | \$46,629 | \$100,000 | | \$146,629 |
| 03-100 | Investigation of the "Early Response" in Functional MRI | Ernst, T. | MED/490 | 8 | | | \$231,159 | \$251,000 | | \$482,159 |
| 03-101 | PET Imaging of Violent Behavior | Wang, G.-J. | MED/490 | 8 | | | \$95,168 | \$100,000 | \$130,000 | \$325,168 |
| 03-103 | PET Study of Acetaldehyde Distribution and Metabolism to Better Understand Alcohol Related Diseases | Li, Zizhong | MED/490 | 8 | | | \$99,469 | \$100,000 | \$100,000 | \$299,469 |
| 03-104 | Hydrogen Atom Transfer from Carbon to Metal - Relevance of a Novel Reaction to Catalyzed Hydrocarbon Conversions | Bullock, M. | CHEM/555A | 6 | | | \$19,643 | \$80,000 | | \$99,643 |
| 03-105 | Radioprotection in D. Radiodurans, a Radiation Resistant Bacterium | Cabelli, D. | CHEM/555A | 10 | | | \$57,100 | \$75,000 | | \$132,100 |
| 03-107 | New Development of Norepinephrine Transporter Radioligands for PET Studies of Substance Abuse, Depression and ADHD | Ding, Y.-S. | CHEM/555A | 8 | | | \$112,074 | \$112,000 | | \$224,074 |
| 03-108 | Experiments in the Short-Wavelength Regime Pertinent to the DUV-FEL Concept | DiMauro, L. | CHEM/555A | 4 | | | \$132,731 | \$132,000 | | \$264,731 |

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2003

| LDRD Proj. No. | Project Title | P.I. | Dept./Bldg. | Theme | Actual | Actual | Actual | Approved Budget | Requested Budget | Total | | |
|-------------------|---|---------------------|-------------|-------|---------|---------|------------|-------------------------|---------------------|--------------|--------------|--------------|
| | | | | | FY 01\$ | FY 02\$ | FY 03 \$ | FY 04 \$ | FY 05 \$ | | | |
| 03-115 | Imaging Tandem Mass Spectrometry for High-Throughput "Fingerprint" Detection of Complex Molecules in Mixtures | Suits, A. | CHEM/555A | 7 | | | \$112,241 | \$113,000 | | \$225,241 | | |
| 03-118 | Condition: Green Chemistry Radiolytic Studies of Ionic Liquids in Service of Security and the Environment | Wishart, J. | CHEM/555A | 7 | | | \$42,416 | \$80,000 | | \$122,416 | | |
| 03-119 | Exploring the Use of Powder Diffraction for Proteins | Allaire, M. | NSLS/725D | 10 | | | \$44,700 | \$80,000 | | \$124,700 | | |
| 03-121 | Element-Resolved Dynamics of Nanoscale Ferromagnets | Kao, C.-C. | NSLS/725D | 5 | | | \$28,641 | \$80,000 | | \$108,641 | | |
| 03-122 | Membrane Biophysics Using Single-Layered Lipid Membrane | Pindak, R. | NSLS/725D | 10 | | | \$29,571 | \$80,000 | | \$109,571 | | |
| 03-127 | High Pressure in Strongly Correlated Materials - An Optical Investigation | Homes, C. | CMP/510B | 5 | | | \$53,679 | \$65,000 | \$11,000 | \$129,679 | | |
| 03-129 | Polyoxometalate Giant Molecules: Novel Synthetic Methods, Characterizations and Potential Applications | Liu, Tianbo | CMP/510B | 6 | | | \$54,426 | \$100,000 | \$46,000 | \$200,426 | | |
| 03-131 | Continuous Spallation Neutron Source | Shapiro, S. | CMP/510A | 4 | | | \$5,192 | Cancelled April 2003 | | \$5,192 | | |
| 03-135 | Exploratory Sol-Gel Synthesis Routes for Perovskite Nanorods and Dots | Vogt, T. | CMP/510B | 5 | | | \$63,285 | \$82,000 | | \$145,285 | | |
| 03-137 | In Situ Soft X-Ray Absorption Spectroscopy Studies of Cathode Materials for Thin Film Lithium-Ion Batteries | Balasubramanian, M. | MSD/480 | 6 | | | \$75,354 | \$83,000 | | \$158,354 | | |
| 03-138 | Functional Bulk Mn-Based Nanocomposites | Lewis, L. | MSD/480 | 5 | | | \$27,917 | \$78,000 | \$42,000 | \$147,917 | | |
| 03-144 | Nanostructured Transition Metal Oxides | Wu, L. | MSD/480 | 5 | | | \$39,172 | \$78,000 | | \$117,172 | | |
| 03-151 | Radio Wave Detection of Ultra High Energy Cosmic Rays | Takai, H. | PHY/510A | 3 | | | \$99,914 | \$125,000 | \$25,000 | \$249,914 | | |
| 03-161 | Generation of Coherent, Femtosecond, High Brightness VUV and X-Ray Using High Order Harmonic Conversion | Srinivasan-Rao, T. | IO/535B | 4 | | | \$129,593 | \$140,000 | | \$269,593 | | |
| 03-162 | New Synthesis Techniques to Control Atomic Defects in Advanced Intermetallic Compounds | Cooley, L. | MSD/480 | 5 | | | \$85,825 | \$144,000 | | \$229,825 | | |
| TOTALS: | | | | | | | \$ 715,016 | \$ 3,970,302 | \$ 7,830,078 | \$ 6,105,218 | \$ 1,099,000 | \$19,719,614 |

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT
2003 PROJECT PROGRAM SUMMARIES

Functional Spectral Signature (FSS) Method for Signal to Noise-Enhancement of Brain Patterns in PET Images

Yeming Ma
C. Felder

01-013

PURPOSE:

Our goal of the project has been to improve the current human brain image analysis tools and technologies and develop new image analysis strategies from three aspects: (1) a software to automate the voxel-level brain image analysis for resampling algorithms; (2) a software to automatically extract brain regions of interest; (3) a novel measure, coefficient of variance, for human brain functional homogeneity and heterogeneity analysis and to build the corresponding software.

By accomplishing the above three goals, we would (1) greatly reduce time and manpower lost to the tedious and intensive manual operation of regions of interest (ROI) extraction and voxel-wise image analysis, especially for resampling that requires analysis on all combinatorial cases; (2) significantly reduce the errors either systematic or non-systematic in brain image processing and analysis; (3) enable the medical researchers to examine not only the mean level of brain functional changes but also changes in brain functional patterns due to disease or drug addiction.

The product of this project is a suite of versatile bioinformatics tools, that will benefit not only medical researchers inside BNL, but also the mental health research society and especially patients with mental disease. It would strengthen our bioinformatics initiatives in order to

compete for future funding in this increasingly important field from NIH, NSF and DOE.

APPROACH:

Resampling implementation based on automated voxel-wise Positron Emission Tomography (PET) analysis. The trend in brain functional image analysis is to perform the statistical test at each voxel level. The advantage of this approach is that one can examine the entire brain instead of the selected brain regions of interest, which would usually cover only a moderate portion of the brain. A public domain software – statistical parametric mapping (SPM) (<http://www.fil.ion.ucl.ac.uk/spm/>) has been developed for this purpose. But the software is not fully automated for each run of the analysis, so researchers must click the buttons and enter the strings manually, which is tedious, labor-intensive and error-prone. Since the software is open source, our plan is to use the existing source code and subsequently build our own graphical user interface with built-in analysis routines that we develop for each subsequent analysis. One could key in a few major parameters and submit the job in batch mode, which enables the more powerful statistical analysis with resampling method on PET data collected at BNL.

Automated anatomical ROI extraction in PET analysis. The traditional brain regions of interest (ROIs) are manually traced by highly trained domain experts on every subject's brain image. Not only is it a very time-consuming task, the outcome is also rather observer-dependent that causes variations among results produced from different research groups. Therefore, we proposed to fully automate this task. The human brain varies in size, aspect ratio, and even in the spatial relationships of their features in addition to the orientation

changes during brain scans of the patients. To eliminate these variations, we first map all brains into a common, normalized brain space – the Talairach brain using SPM. Next we obtain the precise location of common anatomical regions in the Talairach brain from the NIH supported public domain Talairach Daemon database (TD), <http://ric.uthscsa.edu/projects/talairachdaemon.html>. The TD database includes major human brain anatomical structures from the entire cortex to the specific cell regions within the cortex. TD functions as a unidirectional server that a user can only obtain anatomical information for a given Talairach coordinate but not vice versa. So we had to find the inverse mapping to extract the Talairach coordinates of all voxels belonging to each anatomical region in order to automate the ROI procedure based on each anatomical region.

Brain functional heterogeneity study via CV. Traditionally, researchers only examine the average activity level of each brain region of interest (ROI mean). However, some diseases or drugs would render some changes in brain regional mean with different activation patterns. We proposed to develop the analysis of brain functional homogeneity and heterogeneity using the coefficient of variation (CV) as the measure of functional variability. The analysis can be done at both the ROI and voxel level and the algorithms need to be fully developed into more user-friendly software.

TECHNICAL PROGRESS AND RESULTS:

Accomplished Task 1 – software for automated voxel level analysis. The batch mode voxel analysis software we had successfully developed for routine PET image analysis was expanded to accommodate the resampling method that, for the first time, provided the confidence

interval on the activation volume detected by SPM. Figure 1 is a screen shot of the user interface. To date we had applied the resampling analysis on several PET studies [Ref.1, 2003] on the cocaine and alcohol abusers brain function by using this software.

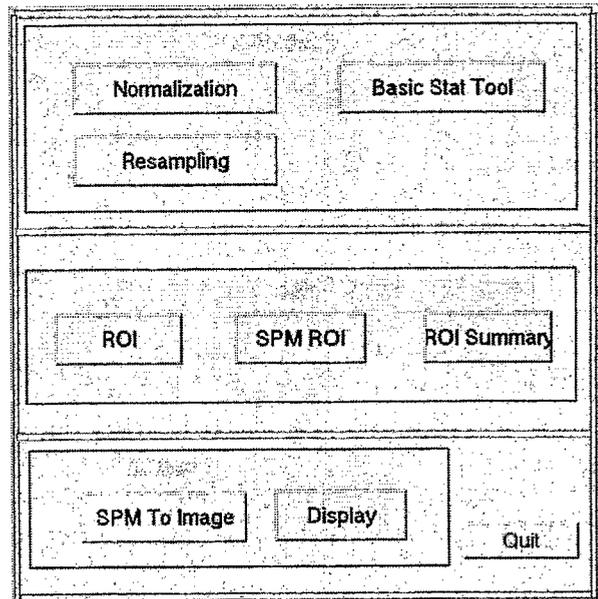


Figure 1

Accomplished Task 2 – automated anatomical region location searcher and quantitative anatomical information extraction software. Figure 2 is the screen shot of the initial page of the software. These ROIs include all major anatomical regions of human brain with various sizes from the entire cortex to the cell regions.



Figure 2

The software allows researchers to locate and visualize the position and shape of each anatomical region starting from the name of each region or by clicking part of the brain regions to receive its anatomical nomenclature. Figure 3 shows part of the extracted cortex displayed on a Magnetic Resonance Imaging (MRI) background by the software and Figure 4 shows the frontal lobe and the occipital lobe displayed on a normalized PET-FDG (fluorine-18-fluorodeoxyglucose) image.

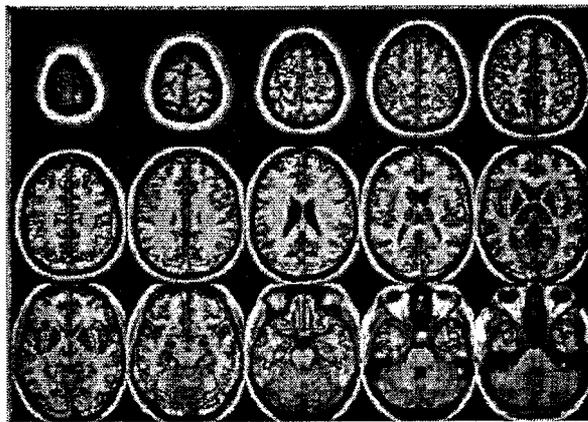


Figure 3

Accomplished Task 3 – automated anatomical region of interest (ROI) value extraction.

We enhanced the existing functions we developed such as the automatic extraction of 5 levels of anatomical ROIs and added several new functions. One of the most significant functions is the automatic extraction function on ROI defined by SPM activation or deactivation regions, which combines the two methods of single-voxel level SPM analysis and multiple-voxel level ROI analysis into one method that obtains a more quantitative description of the brain activation. In Figure 4 we illustrate that in the two highlighted regions on a normalized PET-FDG image of a patient that indicates the patient’s brain metabolic level, the frontal lobe and the occipital lobe. The

software will not only calculate key statistics that we now use to quantify the functional status such as mean, standard deviation and CV but also expandable into new statistics developed as plug-ins in future work. The results produced by the automatic ROI method have been published in [Ref. 3, 2003]. The software provides a framework with room for refinement and expansion into more applications in brain image analysis.

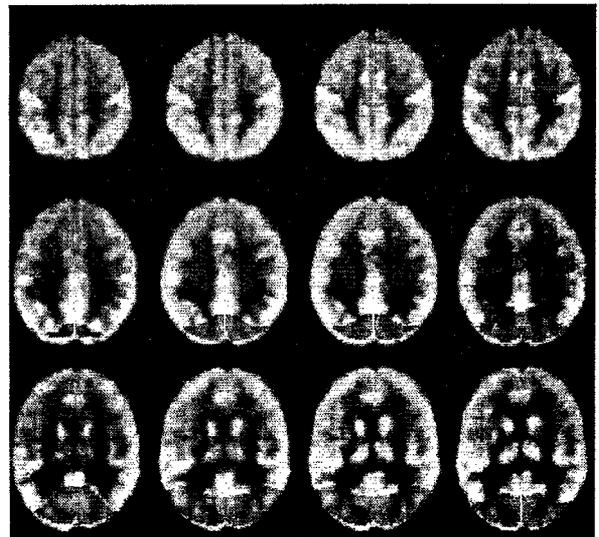


Figure 4

Accomplished Task 4 – analysis tool for functional heterogeneity study. In FY 2001, we accomplished task 3(a): the analysis of brain functional heterogeneity at the ROI level. In FY 2002, we had accomplished task 3(b): the analysis of the functional heterogeneity at the voxel-level and the software for doing this type of analysis. Figure 5 is a screen shot of the original PET image and its corresponding functional heterogeneity image from our newly developed software “BrainCV.”

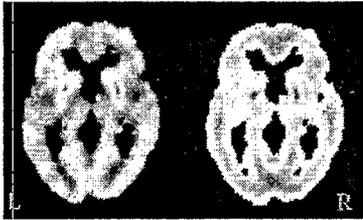


Figure 5

In summary, we have accomplished the following task items in FY 2002-2003: (1) resampling method in SPM by using the automatic batch mode program for PET analysis; (2) automatic extraction function on ROI defined by SPM activation or deactivation regions; (3) (4) multi-resolution analysis of the function homogeneity /heterogeneity analysis method.

In the past year have had two graduate student volunteers, Manlong Rao, Kith Pradhan, and one undergraduate student volunteer, Sean Li, working on this project with us. In addition, we receive advice on the medical aspects from Drs. Nora Volkow, Gene-Jack Wang, and Joanna Fowler at BNL Life Sciences.

SPECIFIC ACCOMPLISHMENTS:

Publications:

Alcohol Increases Brain Functional Homogeneity. Volkow, N. D.; Ma, Y.; Zhu, W.; Li, J.; Mueller, K.; Rao, M.; Wang, G.-J.; Wong, C.; Fowler, J. S. *Psychiatry Research* (2002) (submitted)

Enhanced resting activity of the oral somatosensory cortex in obese subjects. Wang, G. J.; Volkow, N. D.; Felder, C.; Fowler, J. S.; Levy, A. V.; Pappas, N. R.; Wong, C. T.; Zhu, W.; Netusil, N. *Neuroreport.*, 13(9), 1151-1155 (2002) (submitted)

Changes in brain functional homogeneity in subjects with Alzheimer's disease. Volkow, N. D.; Zhu, W.; Felder, C.; Mueller, K.; Welsh, T. F.; Wang, G. J.; de Leon, M. J.; *Psychiatry Res.*, 114(1), 39-50 (2002) (submitted)

Expectation Enhances the Regional Brain Metabolic and the Reinforcing Effects of Stimulants in Cocaine Abusers. N. Volkow, G.-J. Wang, Y. Ma, J. Fowler, W. Zhu, L. Maynard, F. Telang, P. Vaska, Y.-S. Ding, W. Christopher, J. Swanson, *Journal of Neuroscience*, 2003 (submitted)

Relationships of Ethanol Induced Changes in Brain Regional Metabolism and Motor, Behavioral and Cognitive Functions. Zhu, W.; Volkow, N. D.; Ma, Y.; Fowler, J. S.; and Wang, G.-J.; *Journal of Alcohol and Alcoholism*, 2003 (submitted)

Incomplete Recovery of Brain Metabolism in Methamphetamine Abusers with Protracted Abstinence. G.-J. Wang, N. D. Volkow, L. Chang, J. S. Fowler, D. Franceschi, M. Leonido-Yee, M. Sedler, E. Miller, R. Hitzemann, W. Zhu, J. Logan, and Y. Ma, *Journal of Neuroscience Neuroscience*, 2003 (submitted)

Grant application in 2003

"Imaging the Mind" NIH P20 proposal 2nd - time submission in September 2003. PI Dr. Arie Kaufman. (Role on the project: unpaid consultant).

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$85,941 |
| FY 2002 | \$45,085 |
| FY 2003 | \$41,383 |

Development of CZT Array Detector Technology for Synchrotron Radiation Applications

D. Peter Siddons

01-030

PURPOSE:

Establishment of the technology to enhance the capabilities of National Synchrotron Light Source (NSLS) beamlines by providing advanced detector capabilities. In particular, pixellated array detectors 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:

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.

In order to understand the factors limiting the energy resolution of CZT detectors, our efforts were directed to the area of material characterization and detector testing using the NSLS. On the macroscopic scale it seems very hard to find a systematic correlation between performance and material defects. Flood illumination of our detectors results in different performance in terms of energy resolution for adjacent strips or pixels of the same detector. Such a macroscopic study cannot tell what is the role of localized defects, whether a high concentration of Te precipitate in a portion of a strip or a single TE precipitate or some other defect such as a twin or low-angle boundary, it just gives an average of all the effects influencing the performance.

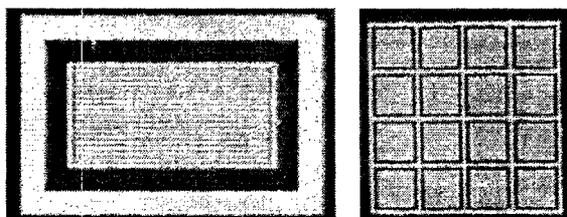
In order to understand the correlation between the fluctuation in collected charge and the microscopic defects and impurities present in the CZT crystal, we used a synchrotron radiation (SR) microbeam, which is a highly collimated, high intensity X-ray beam of transverse dimension of order micrometers, to perform a raster scan of the detector area. In this way it is possible to illuminate an area of the detector comparable to the defect size and determine the performance at each point.

By superposing the performance data on maps of defect location, we will be able to ascertain what defects are deleterious and which ones are benign. It is therefore important that we can determine the 3-D defect conformation in each sample. We therefore have begun defect mapping and performance mapping studies. The most obvious defects are tellurium precipitates and twin boundaries. We have visualized them using infrared (IR) microscopy and we present results of those measurements here.

TECHNICAL PROGRESS AND RESULTS:

In the current year we have made additional improvements in the detectors by optimizing the surface preparation process and by using the optimal combination of bromine and lactic acid for removing surface damage. The fabrication process was described in the previous report, so will not be repeated here. In the previous annual report we also described a pixellated array which consisted of 4 groups of 16 detectors, each 1mm x 1mm, arranged in a square. We have now also produced a lithography pattern in the form of narrow strips. Such a detector would have applications in x-ray diffraction at high photon energies. A large number of detectors of each type were made. The figure below shows examples of detectors made using the two test lithography patterns.

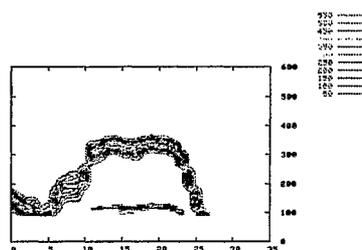
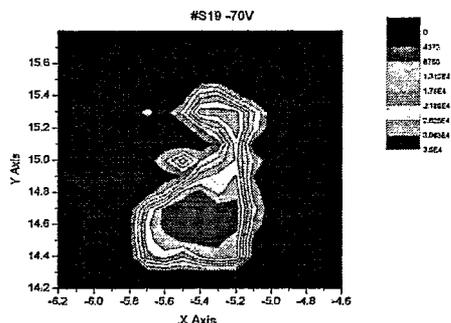
Each consists of 16 detectors, the pixellated one formed of 1mm x 1mm squares and the strip device from 4mm x 100 micrometers strips on a 125-micrometer pitch, surrounded by two guard rings, a wide one which serves to collect surface currents which would otherwise degrade the detector performance. The inner ring electrodes can serve either as a second guard or may be connected to the strips in such a way as to form a coplanar grid structure. This structure is a special arrangement designed to provide an output signal from electrons only, rather than both electrons and holes in combination.



In order to understand the correlation between the position-dependent variations in collected charge and the microscopic defects and impurities present in the CZT crystal, we used a synchrotron radiation (SR) microbeam having dimensions $25\mu\text{m} \times 25\mu\text{m}$, to perform a raster scan of the detector. For our first measurements we used a $50\mu\text{m}$ scanning step. The energy of the radiation source can be set anywhere in a range between 7keV and 50keV. We chose an energy of 30keV for the first set of measurements. Due to the high brightness of the source it is possible to have good statistics in very short times, about 1 second. Therefore, the time to perform a raster scan of the entire ($2 \times 4\text{mm}^2$) area that surrounds the detector is very short, within 40 minutes.

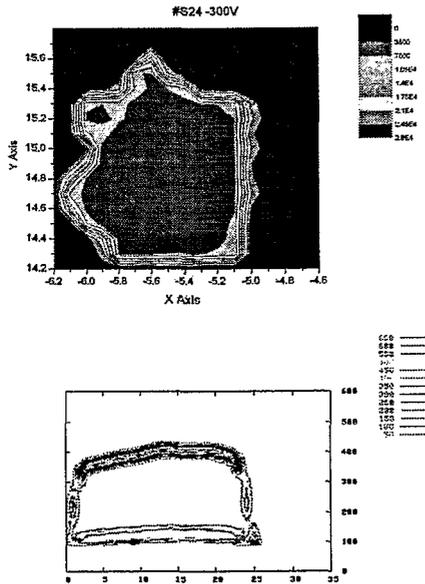
The detector together with the low-level readout electronics is mounted on an x-y precision motor-controlled stage, perpendicular to the incident beam, in such a way that the X-ray beam illuminates the

cathode. This is the case that gives the best energy resolution. The raster scans were performed at several bias voltage values from -250V to -80V .



Our first measurements using this mapping system were made on the square-pixellated device and the figures above illustrate typical results. The counter was set to record all events having the average pulse height. It is seen that, at this value of bias voltage, the pixel shows a quite uniform response. A single line scan through the center of this image, during which complete spectra were recorded at each point, shows a quite uniform region to the right, but a tailing off of the peak height on the left side of the pixel. Reducing the bias voltage (and hence reducing the charge collection efficiency) shows a dramatic change in the picture. Now, the pixel is only half responsive in the 2-D window scan. Again, a line scan of full spectra show that significant charge loss is occurring on the left part of the pixel, as was hinted at in the high bias image. This level of variability is unacceptable if one hopes to use the energy

resolution as a noise-reducing property of the detector.



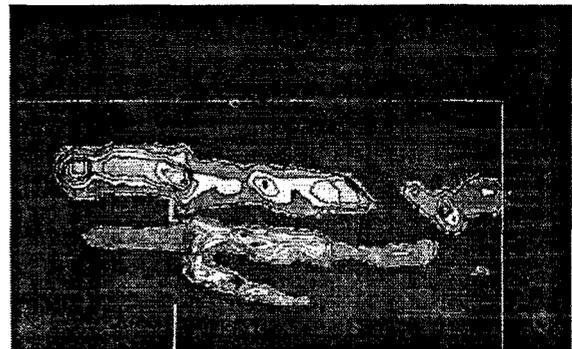
In order to try to identify the defects causing this non-uniformity we interrupted the detector fabrication process just after the lithography step. An IR image taken at this stage reveals the patterned areas superposed on any precipitates in the crystal bulk. This is not possible after metallization, since the metal layer is opaque in the IR. Superposing the intensity contour maps on the IR image generated the following images.

The IR images are the composite of many 0.5mm x 0.5mm images taken one by one and manually stitched together in the computer. It is easy to know the dimensions of any single feature since the dimensions of the lithographic pattern are known. The same set of images was taken for 2 other focal planes: 1mm and 2mm depth. The twin boundary goes all the way down to the back surface. This could be the reason this detector cannot sustain a voltage higher than 270V. Normally for a 2mm thick detector a voltage of 500V is easily applied. An automated motor controlled system together with software to create the 3D image of the

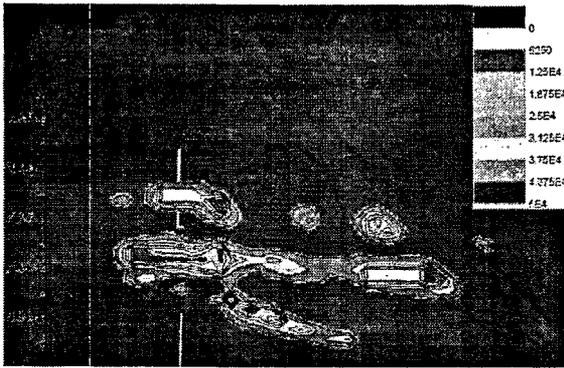
entire crystal is under development. In this way it would be possible to know the position (x,y,z) of each feature (twin boundary or precipitate) in the crystal volume inspected.

This IR image is superposed on the contour map of the number of counts within the nominal photopeak pulse height window.

Below are shown two contours maps of the number of counts within the nominal photopeak pulse-height window at -200V and -140V, for two of the 16 strips. They are far from being uniform; it is possible to see that there are no counts where the twin boundary are located, this in the case of -140V applied. An explanation can be given by saying that the charge trapping is high or the electric field is distorted in that region, or most likely a combination of both effects. When we apply -140V the field is not strong enough to overcome the charge trapping in that region, this is why there is no detectable number of counts. More studies on the electric field distribution will be undertaken. Another very interesting phenomenon that can be observed is the "tail" of detectable counts on the lower part of the detector. In that region there is no metal contact, so one would expect to see no counts. We can postulate the Te precipitates seen in this region provide a conductive path allowing charge generated outside the metallization to be transported and collected at one of the strips. The same behavior is observed in this region when -200V are applied.



(a)



(b)

Number of counts within the nominal photopeak pulse-height window at (a) -200V and (b) -140V

SPECIFIC ACCOMPLISHMENTS:

The technologies and facilities developed under the LDRD have formed the basis for grant proposals, in collaboration with Dr. Ralph James of the Energy, Environment and National Security (EENS) directorate, in the field of Homeland Security, most of which are still pending at the time of this report.

Refereed publications:

“Micro-Scale 2D Mapping of Cadmium-Zinc Telluride Strip Detectors”, Giuseppe S. Camarda, Edson M. Kakuno, Gabriella Carini, A. E. Bolotnikov, G. W. Wright, R. B. James, D. Peter Siddons. Institute of Electrical and Electronics Engineers (IEEE) Transaction Nuclear Science (2003) - in press.

Conferences:

“Cadmium-Zinc Telluride Detector Arrays for Synchrotron Radiation Applications”, Edson Kakuno, Giuseppe Camarda, D. Peter Siddons. NSLS User Meeting, Upton, NY, May 19-21, 2003.

“Cadmium-Zinc Telluride Detector Arrays for Synchrotron Radiation Applications”,

Edson Kakuno, Giuseppe Camarda, D. Peter Siddons. Proceedings of SPIE Vol. 5198, San Diego, August 3-8, 2003.

“Effects of Surface Roughness on Large-Volume CdZnTe Nuclear Radiation Detectors and Removal of Surface Damage by Chemical Etching”, G. W. Wright, G. Camarda, E. Kakuno, L. Li, F. Lu, C. Lee, A. Burger, J. Trombka, P. Siddons, R. B. James. Proceedings of SPIE Vol. 5198, San Diego, August 3-8, 2003.

“Micro-Scale 2D Mapping of Cadmium-Zinc Telluride Strip Detectors”, Giuseppe S. Camarda, Edson M. Kakuno, Gabriella Carini, A. E. Bolotnikov, G. W. Wright, R. B. James, D. Peter Siddons. 13th International Workshop on Room-Temperature Semiconductor X- and Gamma-Ray Detectors, Portland, October 19-25, 2003.

“Factors Limiting the Performance of CdZnTe Detectors,” A.E. Bolotnikov, G. Camarda, G. W. Wright, R. B. James. 13th International Workshop on Room-Temperature Semiconductor X- and Gamma-Ray Detectors, Portland, October 19-25, 2003.

“Surface-Roughness and Injecting Contact Effects on Large-Volume CdZnTe Nuclear Radiation Detectors,” G. W. Wright, G. S. Camarda, A. E. Bolotnikov, M. Groza, A. Burger, R. B. James. 13th International Workshop on Room-Temperature Semiconductor X- and Gamma-Ray Detectors, Portland, October 19-25, 2003.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$106,592 |
| FY 2004 (budgeted) | \$ 68,399 |

New Applications of Circular Polarized VUV-Light (NANO IV)

Elio Vescovo

01-031

Hangil Lee

Steve 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 had been successfully installed and tested at U5UA. (For details see previous LDRD report)

In FY 2002, Dr. Hangil Lee had been hired to work on this project. To complete the project successfully it is mandatory to improve the electron collection efficiency in order to compensate for the decreased photon flux (in going from linear to circular light). This is obtained by substituting the current electron spectrometer with a more efficient one. A new end-station based on an Omicron 125 mm spherical analyzer (the old analyzer was 50 mm) has been designed, built, and assembled at the U5UA beamline.

In FY 2003, the new photoemission apparatus has been commissioned. Besides the increased collection efficiency, the new system constitutes an important improvement of the experimental apparatus in several respects. The energy resolution is considerably improved (about a factor 2). Furthermore, the new vacuum systems have

been equipped with a sample fast-transfer load-lock which considerably reduces the down-time between experiments. The new system is now fully operational.

SPECIFIC ACCOMPLISHMENTS:

(Poster) Hangil Lee, In-Gyu Baek, H.-J. Kim and E. Vescovo, "Manipulating the surface anisotropy in Fe(110) Ultra-thin Films," NSLS User Meeting (2002) (oral)

Hangil Lee, In-Gyu Baek, and E. Vescovo, "Spin-Reorientation Transition in Fe(110): the role of magnetoelastic anisotropy," MMM2002, Tampa, Florida (Nov. 11, 15).

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$23,860 |
| FY 2002 | \$52,904 |
| FY 2003 | \$51,191 |

Prototype Approaches Toward Infrared Nanospectroscopy

G. L. Carr

01-035

L. M. Miller

PURPOSE:

Infrared microspectroscopy with synchrotron radiation is a probe of the local chemical and electronic properties of materials, achieving 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 apertures, 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 data from far-field measurements can be readily interpreted according to standard spectroscopic analysis methods.

The alternative approach is based on near-field techniques where one uses an infrared source or probe having dimensions smaller than a wavelength (and the diffraction limit),

and places the sample in close proximity to this source/probe. The technique is very inefficient, and requires a very high brightness source to achieve an acceptable signal-to-noise. 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 to gain understanding in this area.

Milestones for FY2003 were 1) analyzing how synchrotron light and spectrometer polarization affects microspectroscopy imaging, 2) analyzing imaging performance of attenuated total reflectance (ATR) using high index crystals, 3) developing both the electronic detector readout and mechanical instrumentation for scanning thermal probe microspectroscopy, and performance testing microscopy at long wavelengths.

TECHNICAL PROGRESS AND RESULTS:

In the first year of this project (FY2001), an infrared microspectrometer was interfaced to the U4IR beamline at the NSLS, and the scanning stage was replaced with a higher precision unit. We completed the microscope upgrade by installing a custom silicon beamsplitter that extended the spectral range into the far-infrared. Surprisingly good performance was achieved down to a frequency of 20 cm^{-1} ($\lambda = 500 \mu\text{m}$). This instrument and beamline are now part of the NSLS General User program and are being used by several research groups (NASA, center National de la Recherche Scientific [CNRS], MIT).

In the second year we refined the microspectrometer's capability for collecting far-infrared spectra, and addressed details of the instrument's optical point spread function. We confirmed our diffraction calculations with experimental measurements and even identified a number of previously unknown imaging artifacts that are intrinsic to the Schwarzschild objectives used in infrared microspectrometers. We also began some studies on a non-optical approach to obtaining spatial discrimination by thermal probe microspectroscopy. This approach was first attempted by a group at the University of Leeds and the Daresbury Laboratory in the UK. Basically, the sample itself acts as part of the spectrometer's detector, and the absorption of light is sensed as heat by a microscopic thermometer. We obtained some of the scanning thermal probes (atomic force microscopy [AFM]-type cantilevers) and conducted initial tests during the second year.

In the third and final year we continued our imaging analysis based on diffraction theory, but included aspects of polarization. We discovered that the unusual polarization characteristics of synchrotron radiation produce a double-lobed spot for vertically polarized light, rather than a simple circularly symmetric pattern. Polarization also affects the performance of the spectrometer itself, as well as the sensitivity for grazing incidence methods. We analyzed the attenuated total reflectance (ATR) microspectroscopy method. This technique employs high refractive index materials having the potential for delivering a 2 to 4-fold improvement in spatial resolution. Lastly, we made improvements to the scanning thermal probe method by

designing and producing a custom instrumentation amplifier based on an AC bridge type circuit. We feel that this method offers the best approach to sub-wavelength spatial resolution in the far-infrared spectral range.

In Summary:

- ◆ Obtained spectra for small collections of 6 μm polystyrene spheres at far-infrared ($\sim 50 \mu\text{m}$) wavelengths.
- ◆ Completed diffraction analysis for polarized synchrotron radiation, and ATR methods.
- ◆ Added a special microscopy cryostat for sample cooling to below 10K, consistent with the low energy phenomena commonly investigated in the very far infrared.

SPECIFIC ACCOMPLISHMENTS:

"Synchrotron-based Biological Microspectroscopy: From the Mid-Infrared through the Far-Infrared Regimes," L. M. Miller, G. D. Smith, and G. L. Carr, *Journal of Biological Physics* **29**, 217 (2003).

"Infrared Microscopy Using a Synchrotron Source Offers Improvements for Arts/Science" Research, Smith, G. D. *Journal of the American Institute of Conservation*. in press (2003).

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$33,689 |
| FY 2002 | \$64,030 |
| FY 2003 | \$43,818 |

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

Lisa M. Miller

01-036

C. -C. Kao

PURPOSE:

The objective of this work is to 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 microspectroscopy (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.

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.

Brookhaven National Laboratory initiative 4.1.4, 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:

At the end of FY 2002, Dr. Lin Yang (LDRD postdoctoral fellow) designed and built an SAXS setup on the NSLS insertion device beamline, X21. Drs. Jim Ablett (LDRD postdoctoral fellow) and Lin Yang, in collaboration with DOE-Energy Research Undergraduate Laboratory Fellowship Program (ERULF) student, Jackie Tetenbaum, determined the structure of native and disulfide-reduced soybean trypsin inhibitor using SAXS.

In FY 2003, the structure of phosvitin, a model bone mineralization protein, was determined using SAXS, circular dichroism (CD), and FTIR. In addition, the effects of pressure on bone proteins and bone mineral were studied in a diamond cell with infrared microspectroscopy. Finally, Dr. Jim Ablett began the design and construction of a diamond anvil cell for pressure-induced protein folding studies. In the future, Jim

Ablett (now an NSLS Scientific Associate) will continue the development of the diamond anvil cell for pressure-induced protein folding studies. In addition, he will modify the rapid-mix flow cell for CD and SAXS and extend these techniques to additional protein systems. Follow-on funding has been requested from the DOE-Genomes to Life Initiative to continue this project and extend it to high-throughput screening of protein structures in solution.

SPECIFIC ACCOMPLISHMENTS:

Publications:

N. S. Marinkovic, A. R. Adzic, M. Sullivan, K. Kovac, L. M. Miller, D. L. Rousseau, S. R. Yeh, M. R. Chance. Design and Implementation of a Rapid-Mixer Flow Cell for Time-Resolved Infrared Microspectroscopy. *Rev. Sci. Instr.*, **71**: 4057-60 (2000).

J. Tetenbaum, L. M. Miller. A New Spectroscopic Approach to Examining the Role of Disulfide Bonds in the Structure and Unfolding of Soybean Trypsin Inhibitor. *Biochemistry*, **40**: 12215-9 (2001).

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Infrared Regimes. *J. Biol. Phys.*, **29** (1): 219-230 (2003).

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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.

J. Tetenbaum, L. M. Miller, L. Yang, J. Ablett (2002). Using Synchrotron Light to Study Solution-State Protein Structure, Folding, and Dynamics. Soft Matter and Biophysics Workshop, Tarrytown, NY, Apr 25-27.

Grant Proposal Funded:

NIH-R01, "Metal Ions and Protein Structure in Protein Folding Diseases" 04/01/03 – 03/31/07, \$540,000 (direct costs).

Grant Proposal Pending:

DOE-Genomes to Life Initiative, "High-Throughput Biophysical Analyses of Purified Proteins" 01/01/04 – 12/31/06 \$1,200,000 (direct costs)

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$43,499 |
| FY 2002 | \$43,511 |
| FY 2003 | \$49,620 |

Soft Condensed Matter Probed by Low-energy Resonant Scattering

Wolfgang A. Caliebe

01-038

R. Pindak

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 measuring 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 been proven 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 free-standing 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 C. C. Huang, Andy Cady, Xifeng Han, Zengqiang Liu, and Suntao Wang from the University of Minnesota, where the laser scattering experiments are performed, Philippe Barois from the University of Bordeaux, France, and K. Ema, K. Takekoshi and H. Yao from the Tokyo Institute of Technology, where high-resolution calorimetric measurements are done.

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:

The research of the previous two years (2001 and 2002) concentrated on the study of the structure and phase transition of liquid crystal films. We studied liquid crystal films containing a Cl-atom for the first time with resonant scattering, and got additional

information on the structure. Significant information was also obtained on the structure of films formed by bent-molecules. The experiment in fall 2002 concentrated on precise measurements of the lattice constant of one liquid-crystal compound which exhibits a no-layer-shrinkage effect at the SmA-SmC* transition, and on the nature of the SmA-SmCa*-SmC* phase transition in two different liquid-crystal compounds.

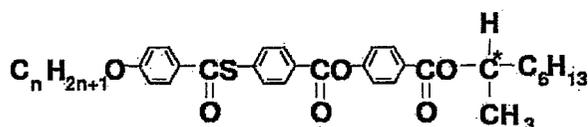


Figure 1. Molecular structure of 10- and 11OTBBB1M7 ($n=10$ and $n=11$, respectively).

In the compound 11OTBBB1M7 in the SmC* phase, we observe satellite peaks around the (002) Bragg peak when the x-ray energy is tuned to the maximum of the white line of the S K-edge in x-ray absorption scan. When the energy is tuned to 20eV above the edge, the satellites disappear. This resonant behavior can be explained with a super-structure, which is associated to the helical pitch formed by the molecules, which are tilted from the film-normal. The distance of the satellites from the main peak gives the pitch, which is around 95 layers below 123°C. Upon heating, between 123°C and 125°C, the pitch rapidly decreases to about 15 layers at 126°C. We also observed a small jump around 124.6°C. This jump indicates the transition to be first-order, which was confirmed subsequently by high-resolution thermal studies.

The helical pitch should result in four satellite-peaks (1. and 2. order) around each principal Bragg peak, but thermal fluctuations and the position of the resonant atom significantly reduce the intensity of the second-order satellites. We studied a mixture of 50% 10OT1BBBM7 and 50% 11OTBBB1M7, which clearly shows the second order peaks.

The no-shrinkage effect was studied in the compound 8422[2F3]. The atom with the highest Z in this molecule is F, which does not allow us to perform resonant scattering, however, the high q-resolution of x-ray diffraction allows us to measure the lattice constant d precisely as a function of temperature.

Upon cooling from the SmA phase, the usual increase in d is observed. The slope changes at temperatures about 4.5K above the phase-transition to the SmC*-phase, and the temperature variation of d turns into a plateau before a small and smooth drop below T_C .

Conventional SmA compounds exhibit a change of about 5% in the same temperature region! This behavior can be explained with a transition from the de-Vries structure to the conventional SmA arrangement. This picture is supported by additional optical studies, but it does not show any thermal signature under high-resolution calorimetric studies.

Finally, significant progress was done on the design of the new light-weight x-ray polarization analyzer. The basic set-up has been specified, and three rotation and two translation stages have been ordered. We now need slit-systems, mount everything and align and test it.

The vacuum-compatible diffractometer is making slow progress, and it is now mounted in a chamber on an optical table. We still have to order feed-throughs for all the cables, Be-windows for the incident x-rays, and build a new oven.

Research on this project will continue with new funding from Nanoscale Science Engineering and Technology (NSET).

SPECIFIC ACCOMPLISHMENTS:

Optical and resonant x-ray diffraction investigations of molecular ordering in chiral liquid crystals. Cady, A., Ph.D. Thesis, University of Minnesota, Minneapolis. (2003)

Optical, resonant x-ray scattering, and calorimetric investigations of two liquid crystal compounds exhibiting the SmA-Sm C*-Sm-C* transitions, Huang, C. C.; Liu, J.; Cady, A.; Pindak, R.; Caliebe, W.; Barois, P.; Nguyen, H.; Ema, K.; Takekoshi, K.; and Yao, H., (accepted for publication) Liquid Crystals. (2003)

Experimental investigations of one liquid-crystal compound exhibiting the no-layer-shrinkage effect near the SmA-SmC* transition, Huang, C. C.; Wang, S. T.; Han, X. F.; Cady, A.; Pindak, R.; Caliebe, W.; Barois, P.; Ema, K.; Takekoshi, K.; and Yao, H., (in preparation for Phys. Rev. E. RC).

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$32,873 |
| FY 2002 | \$50,401 |
| FY 2003 | \$49,422 |

Femto-Seconds Electron Microscope Based on the Photocathode RF Gun

Xijie Wang
Z. L. Wu

01-039

PURPOSE:

The objective of this work is to explore the photocathode RF gun technology for femto-second, time-resolved electron diffraction applications. By taking advantage of higher energy and electron beam energy correlations from the photocathode RF gun, our approach would allow us to break the pico-second time barrier for the first time with electron diffraction.

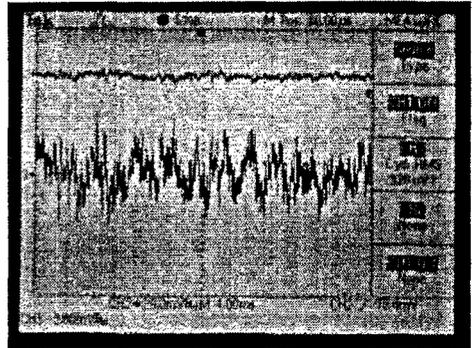
APPROACH:

To realize the femto-second electron diffraction at BNL, we need to demonstrate the feasibility of the technology and scientific cases for femto-second electron diffraction. We continue to make progress in the RF gun technology for femto-second electron diffraction. We organized one seminar on femto-second electron diffraction, hosted a feasibility discussion with experts from BNL's Materials Science Department, Brown University, and the University of Chicago. We established collaboration with Prof. H. Ihee of Korea Advanced Institute of Science and Technology (who used to be at the University of Chicago). We are now exploring the possibility of carrying out the first demonstration experiment in other labs where a photocathode RF gun is operating.

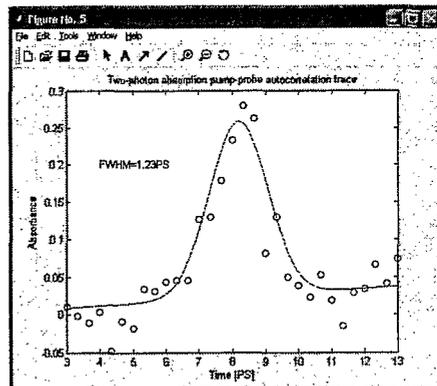
TECHNICAL PROGRESS AND RESULTS:

During FY 2003, significant progress was made in femto-second (fs) laser oscillator, photocathode RF gun construction, and timing jitter studies:

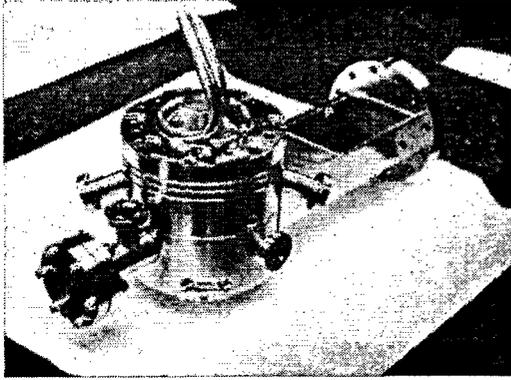
1. Femto-seconds Yb:glass laser oscillator: after successful commissioning the femto-second Yb:glass laser oscillator, we continue to make progress in its performance improvement and characterization. The measured timing jitter of the oscillator is less than 200 fs (FW, figure below). The measurement data is noise limited.



2. UV auto-correlator: We designed and constructed a 266 nm auto-correlator for femto-second laser pulse length measurements based on the two-photon absorption. This device has been used to characterize the Deep Ultra Violet – Free Electron Laser (DUV-FEL) High-Gain Harmonic Generation (HG) output length and demonstration of HG output pulse length control through the seed laser.



3. The photocathode RF gun: We finished construction of the photocathode gun during this fiscal year.



4. Timing jitter analysis: The total time resolution of the femto-second electron diffraction is determined by,

$$(\Delta t)^2 = (\Delta t_{laser})^2 + (\Delta t_e)^2 + (\Delta t_{VM})^2 + (\Delta t_{jit})^2$$

where Δt_{laser} is the laser pulse length, Δt_e is the electron pulse (e-pulse) length, Δt_{VM} is the velocity-mismatch, and Δt_{jit} is the jitter between the pump laser pulse and the probe e-pulse. Δt_{laser} below 100 fs can be obtained routinely. To realize sub-100 fs time resolution, we not only have to reduce the electron bunch length (Δt_e), also Δt_{VM} and Δt_{jit} . Δt_{VM} can be reduced below 100 fs either by increase the electron beam energy above 1 MeV, or special configuration which may lead to significant reduction of the diffraction signal.

In the following, we would like to show (Δt_{jit}) between the pump laser and electron beam can be reduced to below 100 fs with present technologies. Since the same laser will be used for both the pump and electron beam generation, Δt_{jit} is the jitter in the arrival time of the e-pulse relative to that of the pump laser pulse at the scattering point. The main concern is the fact that the timing jitter between the RF system and the laser system (the RF-laser jitter) can be as large as 1 ps. However, the manifestation of the RF-laser jitter in the final timing jitter is negligible for the following reasons. First, instead of the sine function-dependency of the e-beam energy on the time in the RF field, it can be approximated as in a

DC field for the laser-RF jitter to be less than a pico-second due to the rapid acceleration. For an RF-laser jitter of 1 ps, it only generates a jitter less than 10^{-4} in the relative e-beam energy, $(\Delta E/E)_{jit}$. Second, the relativistic effect ($1/\gamma^2$) will further reduce the timing jitter. When v_e approaches the speed of light, c , Δt_{jit} can be estimated by,

$$\Delta t_{jit} \approx \frac{\ell}{c\gamma^2} \left(\frac{\Delta E}{E}\right)_{jit}$$

where γ is $(1-v_e^2/c^2)^{-1/2}$, and ℓ is the distance from the cathode to the scattering point. So the arriving time jitter (Δt_{jit}) of the electron beam will be less than 100 fs for the RF-laser jitter less than 1 ps. The key to reducing the timing jitter below 100 fs is to stabilize the RF amplitude to better than 10^{-4} , which is well within the reach of the present RF technology.

SPECIFIC ACCOMPLISHMENTS:

X. J. Wang, M. Babzien, and Z. Wu, "Electron Beam Based Laser Diagnostics," presented at Workshop on Laser Issues for Electron RF Photoinjectors SLAC, October 23-25, 2002 (SLAC-WP-025).

X. J. Wang, H. Ihee, and Z. Wu, "Femto-second Electron Diffraction based on a Photocathode RF gun," Oral presentation at PAC'03, May 12-16, 2003.

X. J. Wang, "Timing Jitter Issues for the Linac System based on the Photocathode RF Gun Injection System," Oral presentation at the 2003 Free Electron Laser Conference, September 8-12, 2003.

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2001 | \$145,593 |
| FY 2002 | \$ 62,119 |
| FY 2003 | \$ 64,622 |

Human DNA Damage Responses: DNA-PK and p53

Carl W. Anderson

01-051

PURPOSE:

In all cells, DNA double-strand breaks (DSBs) occur spontaneously and are caused by internal stresses as well as exposures to a variety of environmental insults including ionizing radiation, oxidative stress, metals, and natural and man-made genotoxic substances. In vertebrates, DSBs are repaired by two major pathways, homologous recombination (HR) and the non-homologous end-joining (NHEJ) pathway. The mis-repair of DSBs creates mutations and genome rearrangements that may lead to cancer. The objective of this project is to develop and validate methods that will permit a determination of whether mutations and polymorphisms in the NHEJ DNA DSB repair genes result in increased susceptibility to cancer in humans. This objective will be attained through three specific aims. First, we will analyze sequences from several human cell lines surrounding the 86 exons of one of the NHEJ DNA repair genes, *PRKDC*, which encodes the catalytic subunit of the DNA-activated protein kinase, for mutations and polymorphisms. Second, we will 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, we will create and analyze endogenous "knock-in" mutations that alter sites of posttranslational modifications in the murine p53 tumor gene. As described below, 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. The sequence of the human *PRKDC* gene and other NHEJ genes, as appropriate, will be validated by analyzing a small number of cell lines that exhibit normal NHEJ function and one cell line that does not. These results are expected to provide necessary preliminary results to support proposals to the NIH or DOE for NHEJ gene polymorphism discovery.

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, NCI, 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:

During FY 2003, analysis of the human KU80 gene for polymorphisms was completed. The Ku80 gene has 20 exons ranging in size from 49 to 249 bp (excluding exon 1). Primers for PCR amplification of ~500 bp segments were designed and used to analyze DNA from four established cell lines that are commonly used in research: HeLa (ATCC CCL-2), from a cervical carcinoma, A549 (ATCC CCL-185), from a lung adenocarcinoma, M059J (ATCC CRL-2365), from a malignant glioblastoma, and M059K (ATCC CRL-2366) from the same glioblastoma. M059J cells lack DNA-PK activity due to a frame shift mutation in exon 32 of the *PRKDC* gene. As for Ku70, no coding polymorphisms were found in the 20 Ku80 exons for these four cell lines, and no polymorphisms were found in the amplified segments containing Ku80 exons 2, 9, 10, 15, or 16. Each of the other amplified segments exhibited at least one polymorphic locus in at least one cell line. All but one of these were in non-coding sequence. HeLa cells, but not A549, M059J, or M059K were heterozygous (G and A) at the third position of a threonine codon in exon 14. Similarly, exons 2 through 85 of the gene for DNA-PKcs have been analyzed from the same four cell lines. Only HeLa cells had a coding polymorphism; it was a T-to-C change in exon 73 that changes an isoleucine codon to a threonine codon in one allele.

Efforts continued to be concentrated on analyzing the role of posttranslational modifications in regulating p53 activity. Modification-specific antibodies were used to characterize the phosphorylation and acetylation of human p53 in response to genotoxic (UV, IR and adriamycin) and non-genotoxic (PALA, taxol, nocodazole)

stress in cultured human cells at 14 known modification sites. In A549 cells, phosphorylation or acetylation was induced at most sites by the three DNA damage-inducing agents, but significant differences between agents were observed. IR-induced phosphorylation reached a maximum 2 h after treatment and returned to near pretreatment levels by 72 h; UV light and adriamycin induced a less rapid but more robust and prolonged p53 phosphorylation which reached a maximum between 8 and 24 h, but persisted (UV) even 96 h after treatment. Ser³³, Ser³⁷, Ser⁴⁶ and Ser³⁹² were more efficiently phosphorylated after exposure to UV light than after IR. The non-genotoxic agents PALA, taxol and nocodazole induced p53 accumulation and phosphorylation at Ser⁶, Ser³³, Ser⁴⁶ and Ser³⁹². Some phosphorylation at Ser¹⁵ also was observed. Modifications occurred similarly in the HCT116 human colon carcinoma cell line. Analysis of single site mutant p53s indicated clear interdependencies between N-terminal phosphorylation sites, which could be classified in four clusters: Ser⁶ and Ser⁹; Ser⁹, Ser¹⁵, Thr¹⁸ and Ser²⁰; Ser³³ and Ser³⁷; and Ser⁴⁶. These data suggest that p53 phosphorylation is regulated through a double cascade involving both the activation of secondary, effector protein kinases as well as intermolecular phosphorylation site interdependencies that check inappropriate p53 inactivation while allowing for signal amplification and the integration of signals from multiple stress pathways.

The ataxia-telangiectasia mutated (ATM) protein kinase is activated in response to ionizing radiation and activates downstream DNA-damage signaling pathways. Although the role of ATM cellular responses to ionizing radiation has been well characterized, its role in response to other DNA-damaging agents is less well defined.

Previously, others had shown that genistein, a naturally occurring isoflavonoid, induced increased ATM protein kinase activity, ATM-dependent phosphorylation of p53 on serine 15 and activation of the DNA-binding properties of p53. During FY 2003, it was shown that genistein also induces phosphorylation of p53 at serines 6, 9, 20, 46, and 392, and that genistein-induced accumulation and phosphorylation of p53 is reduced in two ATM-deficient human cell lines. Also, it was shown that genistein induced phosphorylation of ATM on serine 1981 and phosphorylation of histone H2AX on serine 139. The related bioflavonoids, daidzein and biochanin A, did not induce either phosphorylation of p53 or ATM at these sites. Like genistein, quercetin induced phosphorylation of ATM on serine 1981, and ATM-dependent phosphorylation of histone H2AX on serine 139; however, p53 accumulation and phosphorylation on serines 6, 9, 15, 20, 46 and 392 occurred in ATM-deficient cells, indicating that ATM is not required for quercetin-induced phosphorylation of p53. These data suggest that genistein and quercetin induce different DNA-damage induced signaling pathways that, in the case of genistein, are highly ATM-dependent but, in the case of quercetin, may be ATM-dependent only for some downstream targets.

To determine the physiological functions of p53 phosphorylations in regulating p53 stability and activity, efforts to introduce single as well as double serine to alanine encoding missense mutations into the endogenous p53 gene of mice were continued in collaboration with others. To test the effect of phosphorylation at Ser18 and Ser23 in regulating p53-dependent activities, during FY 2003 p53^{S18,23A} double mutant mice were created and analyzed in thymocytes after IR and in mouse embryo fibroblasts (MEFs) after UV. Previously,

cells containing single serine-to-alanine substitution mutants at these positions had been constructed. p53 was induced to similar maximum levels in p53^{S18A}, p53^{S23A} and in wildtype thymocytes after IR, whereas in p53^{S18,23A} cells, p53 stability was significantly impaired. Unexpectedly, Western blotting analyses showed that p53 was induced to higher levels in p53^{S18A} MEFs than in wildtype, p53^{S23A} or p53^{S18,23A} MEFs. Since Mdm2 plays a major role in regulating p53 stability, the p53-Mdm2 interaction was analyzed by a co-immunoprecipitation assay at different time points after UV radiation and was found to be weaker in p53^{S18A} MEFs than that in wildtype and p53^{S23A} MEFs, thus providing a basis for the higher protein levels of p53 in p53^{S18A} MEFs. To further characterize the reduced p53-Mdm2 interaction in p53^{S18A} MEFs after UV radiation, the induction of Mdm2 mRNA in p53^{S18A} and wildtype MEFs was analyzed by quantitative real-time polymerase chain reaction (PCR). In contrast to the findings that higher Mdm2 mRNA levels were detected in p53^{Ser18Ala} thymocytes after IR, Mdm2 mRNA levels were significantly lower in p53^{Ser18Ala} MEFs after UV or IR radiation than in single mutant or wildtype MEFs. Taken together, these findings may account for the higher protein levels of p53 in p53^{Ser18Ala} MEFs after DNA damage and indicate that Ser18 phosphorylation plays a cell type-specific role, at least in relation to the transcriptional regulation of Mdm2. These studies thus demonstrated that Ser18 and Ser23 phosphorylation play important but redundant roles in regulating p53 stability in response to genotoxic stresses in certain cell types, in part through differential effects in regulating p53-mediated transcription.

SPECIFIC ACCOMPLISHMENTS:

Publications:

Mauser, A.; Saito, S.; Appella, E.; Anderson, C. W.; Seaman, W. T.; and Kenney, S. The Epstein-Barr virus immediate-early protein, BZLF1, regulates p53 function through multiple mechanisms. *J. Virol.* 76, 12503-12512 (2002).

Saito, S.; Yamaguchi, H.; Higashimoto, Y.; Chao, C.; Xu, Y.; Fornace, Jr, A. J.; Appella, E.; and Anderson, C. W. Phosphorylation site interdependence of human p53 posttranslational modifications in response to stress. *J. Biol. Chem.* 287, 37536-37544 (2003).

Anderson, C. W.; and Appella, E. Posttranslational modifications of p53:

Upstream signaling pathways. In: *The p53 Tumor Suppressor Pathway and Cancer*, G. P. Zambetti, Editor, Kluwer Academic Plenum Publishers (2003, in press).

Ye, R.; Goddarzi, A. A.; Kurz, E. U.; Saito, S.; Higashimoto, Y.; Lavin, M. F.; Appella, E.; Anderson, C. W.; and Lees-Miller, S. P. The isoflavonoids genistein and quercetin activate different stress signaling pathways as shown by analysis of site-specific phosphorylation of ATM, p53 and H2AX. *DNA Repair* (2003, in press).

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2001 | \$167,158 |
| FY 2002 | \$124,603 |
| FY 2003 | \$ 61,706 |

Charge Transfer on the Nanoscale: Theory

Marshall D. Newton

01-087

PURPOSE:

The objective of this project is to model the energetic and electronic structural characteristics controlling 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 (≥ 100 atoms and ≥ 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 evolving plans for the BNL 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 formulated for study of metal-mediated electronic and vibronic coupling in extended conducting junctions based on Green Function methods.

TECHNICAL PROGRESS AND RESULTS:

FY 2002

The influence of electronic structural effects on tunneling propensities in conductive junctions was modeled, with new emphasis on the role of nuclear modes (both molecular modes of the junction and low-frequency modes of background polar media) in modulating the coupling underlying electron tunneling. Fluctuations controlling thermal activation of charge transfer in polymeric systems with low charge-injection gaps (≤ 1 eV, as e.g., in the case of DNA duplexes) were shown to exert a strong modulating influence on tunneling, with detailed behavior depending on the precise charge transfer characteristics (charge separation vs. charge shift, electron vs. hole carriers).

FY 2003

The work reported for FY 2003 was performed by a Research Associate (Dr. Luhong Wang). High-level ab initio electronic structure calculations yielded

quantitative estimates of the interaction energy between adjacent molecules in an ordered monolayer film of alkane thiolates on a gold surface. Model clusters were employed, based on the full monolayer/substrate system, with one or two ethylthiolate molecules, both with and without the underlying nearest-neighbor gold atoms. The calculations led to the following conclusions regarding adsorbate-adsorbate interactions (i.e., departures from pure 'single molecule' behavior). Even with 5 Å separating neighboring alkane chains, electronic overlap leads to substantial energy dispersion (~.2). Furthermore, cooperative charge transfer from the adsorbate to the substrate is attenuated by 25% in proceeding from the limit of a single isolated adsorbate to a pair of neighboring ones. These nonlinear features are of general interest for elucidating monolayer films and rationalizing related band structure calculations for full monolayer systems.

SPECIFIC ACCOMPLISHMENTS:

Funding PI in DOE NSET grant: "Charge Injection and Transport in Nanoscale Materials," funded for the period FY 2001-2004; PI in BNL Center for Functional Nanomaterials, funded, Spring, 2002.

Publications

Rapid Electron Tunnelling, H. D. Sikes et al, *Science* **291**, 1519-1523 (2001).

Distance-Dependent Activation Energies for Hole Injection, Davis, W. B.; et al, *J. Amer. Chem. Soc.* **124**, 2422-23 (2002).

Application of the Linearized MD Approach for Computing Equilibrium Solvation Free Energies, M. V. Vener et al, *J. Phys. Chem. A* **106**, 13078 (2002).

Electronic Coupling of Donor/Acceptor Sites, M. D. Newton in *ACS Symposium Series* **844**, 196 (2003).

Heterogeneous Electron Transfer Kinetics for Ruthenium and Ferrocene Redox Moieties, J. F. Smalley et al, *J. Am. Chem. Soc.* **125**, 2004 (2003).

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Distance Dependence of Electron Transfer Across Peptide Structures, Y. -G. K. Shin, et al, *J. Amer. Chem. Soc.* **125**, 3722 (2003).

Electronic Coupling in Electron Transfer and the Influence of Nuclear Modes, M. D. Newton *Theoretical Chemistry Accounts* (in press).

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$43,063 |
| FY 2002 | \$54,429 |
| FY 2003 | \$17,512 |

High Resolution Magneto-optical Study of Magnetic Nanostructures, Nanocomposite Functional and Superconducting Materials

Qiang Li

01-093

PURPOSE:

A high resolution magneto-optical imaging (MOI) device has been developed to provide a novel and versatile characterization tool for investigating the collective behavior of magnetic interaction in various types of magnetic nanocomposite materials and superconductors. The success of this technique will greatly broaden BNL's capability of conducting fundamental scientific studies and pursuing practical application of various functional materials. The MOI system built at BNL in this proposal is capable of performing both static and dynamic studies of magnetic structures at resolution of a few μm at temperatures from 4.2 K to 450 K under magnetic fields.

APPROACH:

One of the greatest challenges in the studies of magnetic properties in various materials is to develop a versatile technique being able to "visualize" the static and dynamic interaction of magnetic structures at wide range length scales. Based on the magneto-optical Faraday effect, the MOI technique allows for a nondestructive and direct observation of changes in local magnetic structures at scale of micrometer to millimeter. Using the magneto-optical effect, we are able to image, as well as study the phenomena associated with, the nucleation of various magnetic domains, domain wall motion, and magnetic flux motion in superconductors. Another unique

strength of this technique is being able to study the dynamic behavior of magnetic properties and its interaction with the 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 transmission electron microscopy, magnetic force microscopy, x-ray scattering and the diffraction method.

TECHNICAL PROGRESS AND RESULTS:

In FY 2001, 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. We custom-designed and installed 1) a low vibration, liquid helium continuing flow cryostat with Janis Corp which was used for temperature control under the microscope; 2) a turbo-pump based vacuum system and incorporated it with the temperature control system; 3) a copper coil magnet for the cryostat capable of producing up to 1000 Oe magnetic field.

In FY 2002, we put the system in a milestone test by imaging the magnetic field distribution profile in a newly discovered MgB_2 superconducting film. The stability and reproducibility of this MOI system surpassed all the performance parameters we had expected from an optical microscope. We found that our homemade instrument can be operated continuously from 450 K down to 4.2 K and under magnetic fields up to 1000 Oe with excellent stability. We also made several improvements later on and studied

the exchange bias in a thin film dispersion of MnO nanocrystallites in Co.

In FY 2003, we used this MOI system extensively for studying the flux motion in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) thin films. The following examples highlight some of the results we obtained with this MOI system.

1) Direct observation of transition from flux pinning to weak link behavior in YBCO films induced by the substrate defects.

The behavior of magnetic flux motion in a series of YBCO films grown on crystalline LaAlO_3 (LAO) substrates was studied using MOI techniques. A transition from flux pinning to weak link behavior was directly observed as the film thickness increases. We found that a flux enters the thick superconducting YBCO films ($1.6 \mu\text{m}$) easily in the area corresponding to the twins on the substrates, in a striking contrast to the case in the thin YBCO films ($0.2 - 0.8 \mu\text{m}$), where a uniform flux penetration was found. The observed transition was explained by the change in the structural defects induced in the overlying YBCO films by the motion of twins on the LAO substrate at high deposition temperature. Our results indicated that the substrate-induced defects can strongly influence the critical current carrying capacity of YBCO coated conductors.

2) Magneto optical studies of YBCO thick films in the critical state.

We performed magneto optical studies of the critical state in YBCO thick films prepared using BaF_2 *ex-situ* post reaction process. A distinctive fractal propagation pattern was observed as the magnetic flux entered the superconducting films (Figure 1), in a striking contrast to the behavior

expected of a uniform type II superconducting film in the critical state. However, by averaging the flux density over a certain length scale, we found that flux penetration can be described with the standard Bean critical state model. The temperature dependence of critical current density J_c was obtained by applying the Bean model to the averaged flux profiles, and found it to be in good agreement with those obtained by direct transport measurements.

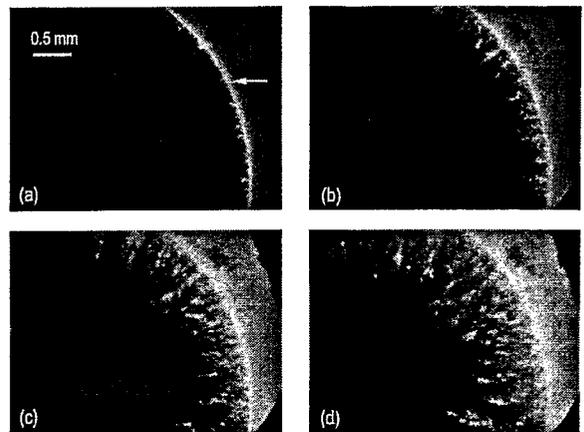


Figure 1. Magneto-optical images of magnetic flux penetration into a zero-field-cooled YBCO thick film circular disk at 40 K, where the arrow indicates the disk edge. The respective images were taken at $B_a = 12.5$ mT (a), 25 mT (b), 37.5 mT (c), and 50 mT (d).

3) Reversal of thickness dependence of J_c in YBCO thick films.

Critical current density J_c as a function of temperature T and magnetic field H was studied for high quality YBCO films with thickness $d = 0.2, 1, \text{ and } 3 \mu\text{m}$ by means of magnetization and MOI measurements of a circular disk in a perpendicular field. We found that the thickness dependence of $J_c(H)$ for the YBCO thick films reverses at high fields for $T > 50$ K, where the $0.2 \mu\text{m}$ -thick film carries significantly lower $J_c(H)$ than the $3 \mu\text{m}$ -thick film at high fields, even though the zero- or low-field

J_c for the 0.2 μm -thick film is more than twice the value for the 3 μm -thick film

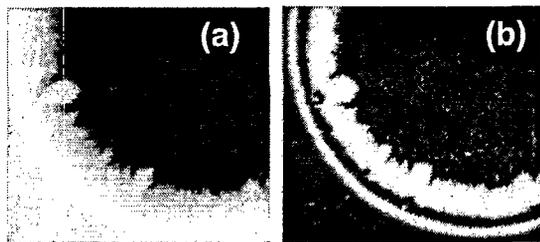


Figure 2. Magneto-optical images of the same area of a 3.0- μm -thick YBCO disk (O.D. = 5.3 mm) at 4.2 K. (a) flux penetration into the disk at external field $\mu_0 H_{\text{ext}} = 0.1$ T applied to the zero-field-cooled sample; (b) flux trapping in the remnant state after $\mu_0 H_{\text{ext}}$ was reduced from 0.1 T to zero.

SPECIFIC ACCOMPLISHMENTS:

Publications:

"Magneto-Optical Studies of YBCO Thick Films in the Critical State," Z. X. Ye, Qiang Li, M. Suenaga, and V. F. Solovyov, to appear in the book of "Magneto-Optical Imaging" T. H. Johansen, Ed., (Kluwer, London, 2004).

"Reversal of Thickness Dependence of Critical Current Density $J_c(T, H)$ in YBa₂Cu₃O₇ Thick Films," Qiang Li, M. Suenaga, Z. Ye, S. R. Foltyn, and H. Wang, submitted to Appl. Phys. Lett.

"Microstructure of Superconducting MgB₂," Y. Zhu, Qiang Li, L. Wu, V. Volkov, G. Gu, and A. R. Moodenbaugh, A book chapter in the book of Studies of High Temperature Superconductors: Advances in Research and Applications V. 38, A. V. Narlikar, Ed., (Nova, Huntington, NY, 2002).

"Thickness Dependence of ac Losses in Circular Disks of YBa₂Cu₃O₇ Films in Perpendicular Magnetic Fields," M. Suenaga, Qiang Li, Z. Ye, S. R. Foltyn, M.

Iwakuma, K. Toyota, F. Funaki, S. R. Foltyn, H. Wang, and J. R. Clem, J. Appl. Phys. (in press)

"ac Losses in Circular Disks of Thin YBa₂Cu₃O₇ Films in Perpendicular Magnetic Fields," M. Suenaga, V. F. Solovyov, Q. Li, Z. Ye, and H. J. Wiesmann, M. Iwakuma, M. Fukui, K. Toyota, and F. Funaki, T. H. Johansen, D. V. Shantsev, and J. R. Clem, J. Appl. Phys. Vol. 94, 502 (July 2003)

"High Critical Current Density in Robust MgB₂/Mg Nano-Composites," Qiang Li, G. D. Gu, and Y. Zhu, Appl. Phys. Lett., vol. 82, 2103, (March 2003)

"Magneto-Optical Studies of Critical States in c-axis Oriented MgB₂ Thin Film and Bulk MgB₂/Mg Nano-Composites," Zuxin Ye, Qiang Li, G. D. Gu, J. J. Tu, W. N. Kang, Eun-Mi Choi, Hyeong-Jin Kim, and Sung-Ik Lee, IEEE trans on Appl. Supercon. Vol. 13, 3722, (June 2003)

"Comparative Studies of MgB₂/Mg Nano-Composites and Press-Sintered MgB Pellets," Qiang Li, L. Wu, Y. Zhu, A. R. Moodenbaugh, G. D. Gu, M. Suenaga, Z. X. Ye, and D. A. Fischer G. D. Gu, and Y. Zhu IEEE trans on Appl. Supercon. Vol. 13, 3051, (June 2003)

"Fractal Growth of Magnetic Flux Penetration in Porous Superconductors," Z. X. Ye, Qiang Li, M. Seunaga, and V. F. Solovyov, W. Si, and P. D. Johnson, to be submitted to Phys. Rev. Lett

"Thickness Dependence of Critical Current Density of YBa₂Cu₃O₇ Films by Transport Self-field Measurements," M. Suenaga, Qiang Li, and S. R. Foltyn, to be submitted to Appl. Phys. Lett.

“Direct Observation of Transition from Flux Pinning to Weak Link Behavior in YBa₂Cu₃O₇ Films Induced by the Substrate Defects,” Z. X. Ye, Qiang Li, Y. Zhu, W. Si, P. D. Johnson, to be submitted to Phys. Rev. B

Presentations:

“MOI Studies of Interplay of Flux Propagation and Structural Disorder in Superconducting YBCO Films,” Qiang Li (Invited), NATO Advanced Research Workshop, Magneto-Optical Imaging 28-30 August 2003, Øystese, Norway.

“Magneto-optical Imaging of Magnetic Structure in Superconductors,” Qiang Li, APS March Meeting Austin, TX, March 3-7, 2003

“Magneto-optical Studies of Critical States in A YBCO Thick Film,” Z. Ye APS March Meeting Austin, TX, March 3-7, 2003

“Magneto-Optical Imaging of Flux Pinning Characteristics in YBCO Thick Films Grown by PLD and BaF₂ ex-situ Processes,” Qiang Li, MRS Fall Meeting, Boston, Dec. 1-5, 2003

“Magneto-Optical Studies of Thickness Dependence of Flux Pinning in YBCO Films Grown on Twinned LaAlO₃ Substrates,” Z. Ye, and Qiang Li, MRS Fall Meeting, Boston, Dec. 1-5, 2003

“Superconducting and Microstructural Properties of MgB₂/Mg Nano-Composites,” Qiang Li. Invited talk Applied Superconductivity Conference, Houston USA, Aug. 4-9, 2002

“Magneto-Optical Studies of Critical States in c-axis Oriented MgB₂ Thin Film and Bulk MgB₂/Mg Nano-Composites,” Z. Y,

Qiang Li, et.al. Applied Superconductivity Conference, Houston, USA, Aug. 4-9 2002

“Critical Current, Flux Pinning and Microstructure of Superconducting MgB₂/Mg Nano-composites and MgB₂ Films,” Qiang Li, et. al. APS March Meeting, Indianapolis, In, March 18-22, 2002

“Superconducting and Microstructural Properties of MgB₂/Mg Nano-Composites,” Qiang Li, MRS Fall meeting, Boston, Nov. 26-30, 2001

Two presentations given related to this project in Review of Division of Materials Science Program - DOE BES Program Review: May 6, 2002:

“Superconducting and Microstructural Properties of High-TC and MgB₂ Superconductors,” Presenter: Qiang Li

“Magneto-optical Studies of Superconductors and Magnetic Materials,” Presenters: Qiang Li and Z. X. Ye

LDRD FUNDING:

| | |
|---------|----------|
| FY 2001 | \$32,748 |
| FY 2002 | \$45,797 |
| FY 2003 | \$26,000 |

Crystallization and X-Ray Analysis of Membrane Proteins

DaXiong Fu

02-002

PURPOSE:

The purpose of this project is to 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. Toward these ends, we will proceed from gene cloning through protein expression, purification and crystallization toward x-ray analysis and structural determination in a three-year timeline. This proposed research meets the general characteristics of the LDRD program in the following three ways. (1) Transmembrane active processes are fundamental and ubiquitous biological phenomena that have not yet been studied at a chemical level due to a lack of a general methodology for crystallization of membrane proteins. This project will enhance the ability of the Laboratory in this forefront area of Life Sciences. (2) Insights gained during our recent crystallization and structural determination of an integral membrane channel resulted in new hypotheses and new concepts that are needed to be further tested and generalized. (3) One major focus of this project is to crystallize and solve the structures of membrane transporters involved in the process of detoxification of heavy metals. Bioremediation is one of DOE's focuses.

APPROACH:

The central idea revolves around the considerations for dual physicochemical properties of membrane proteins that are

destined to the polar, non-polar environments of the lipid bilayer. This biphasic feature of membrane proteins makes structural analysis almost entirely inaccessible to current biochemical and biophysical approaches that have been developed for studying polar globular proteins. In this proposed research, we will explore new approaches to convert membrane proteins to the equivalents of globular proteins using detergents and other amphipathic reagents. We will also 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.

TECHNICAL PROGRESS AND RESULTS:

All milestones in FY 2001 and FY 2002 were met as planned, including cloning eight representative membrane channels and transporters from *Escherichia coli.*, conducting mini-scale protein expression and purification, defining solubilization conditions to extract each of the eight proteins from membranes and optimizing protein expression.

Starting from FY 2002, our experiments were focused upon YiiP, a heavy metal transporter that showed excellent solution stability in certain detergent conditions. The transport function of YiiP was characterized by liposome reconstitution and transmembrane flux/uptake measurements. The metal ion binding to YiiP was examined by isothermal titration calorimetric analysis. The secondary structure of YiiP was determined in detergent micelles by circular dichroism spectroscopy and in lipid bilayer by FTIR spectroscopy. The membrane topology of YiiP was examined using

combined techniques of protease digestion, mass spectrometric analysis and site-directed chemical labeling. The purification of YiiP was streamlined and scaled up to 100 mg range. Crystallization screening for YiiP was initiated and several possible leads began to emerge.

We have met most milestones planned for FY 2003. Initial crystallization conditions for the metal transporter YiiP and its isoform ZitB were defined. Fine grid screenings were carried out to optimize crystallization conditions. These experiments yielded small diffracting ZitB crystals. Cryo-conditions to flash-freeze ZitB crystals were also determined and initial x-ray analysis is underway. In addition, structure-function studies yielded several important findings regarding the mechanism of the metal transporter. We developed a novel 96-well fluorescence-based assay to identify a determinant residue in YiiP for metal binding. The mechanism of metal binding was further examined using EXAFS and ^{113}Cd NMR analyses. Furthermore, we used a multi-angle light scattering technique, in combination with chemical cross-linking, to determine the oligomeric state of YiiP. The functional implications of these findings were further investigated by mutagenesis and transport assay using a purified reconstituted system.

We are expected to meet all the planned milestones at the end of FY 2003.

So far our studies on YiiP/ZitB allowed developments of a general approach for membrane protein purification, crystallization and functional analysis.

SPECIFIC ACCOMPLISHMENTS:

One paper was submitted (Daniels, B. V., Jiang, J.-S., and Fu, D. Crystallization and preliminary crystallographic analysis of the *Escherichia coli* water channel AqpZ. *Acta Cryst.*, 2003, submitted) and another one will be submitted this month (Chao, Y. and Fu, D. Kinetic analysis of an *Escherichia coli* zinc transporter ZitB. To be submitted to *J. Biol. Chem.*). In addition, two more papers are in preparation and several projects are making rapid progress. Heavy metal transporters are of critical importance both in human health and in bioremediation. Preliminary studies with metal transporters will allow us to apply for another RO1 NIH grant in mid-FY 2004. These results are not reports of pre-FY 2003 work.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$380,454 |
| FY 2003 | \$396,551 |
| FY 2004 (budgeted) | \$414,400 |

***In Vitro* Investigation of the DNA Double Strand Break Repair Mechanism by Non-Homologous End-Joining in the Context of Chromatin**

Elena S. Lyman

02-003

PURPOSE:

The DNA double-strand breaks (DSBs) cause chromosomal fragmentation and, if not repaired, may result either in cell death or cancer. The DSBs occur under cell exposure to genotoxic stress (e.g., oxidative stress, chemotherapy, ionizing radiation) as well as under normal physiological conditions. The predominant mechanism of DSB repair in human is non-homologous end-joining (NHEJ). The defects in NHEJ have been implicated in a number of pathological conditions including severe immuno-deficiency, tumorigenesis, radiosensitivity, accelerated morbidity, mental and growth retardation. Despite the progress in NHEJ research, there is still no precise mechanistic understanding of DSB repair *in vivo*, which to a great extent, is due to the lack of an appropriate *in vitro* model.

This project is aimed at the development of a novel, advanced and physiologically relevant model for studying molecular mechanisms of DSB repair. The model will be based on chromatin templates, providing the closest possible approximation of the *in vivo* conditions. This model will allow investigating the most fundamental aspects of DNA damage and repair, which are not amenable to all presently available *in vitro* models based on the usage of free DNA. Specifically, we will address the following questions: (1) how DNA repair complex assembles on the site of damage in the

context of chromatin; (2) what type of chromatin remodeling complex assists this process; 3) which proteins mediate communication between these two complexes. We anticipate that the development of the unique and advanced experimental system for studying DSB repair *in vitro* as well as demonstration of its potency will help to secure the follow-on funding for further, in depth investigations of the mechanisms of DSB repair in human cells.

APPROACH:

1. To reconstitute the NHEJ protein complex *in vitro*, we will clone and express all of its components as recombinant proteins: DNA-PKcs, Ku70, Ku80, Rad50, Mre11, Nbs1, Ligase4, and XRCC4. We will also express the proteins that have been shown to interact with the NHEJ complex and to regulate its function: C1D, HMG1, and HMGI. The proteins will be purified using conventional and affinity chromatography. As an additional benefit, having these proteins purified will enable structural characterization of the NHEJ repair complex.

2. To reconstitute human physiological chromatin *in vitro*, we will develop a novel assembly system based on human recombinant chromatin remodeling complex. Our system will be composed of cloned human components: ACF1, ISWI (2H or 2L), TopoI, Chrac15, Chrac17, DNA and histones purified from human cells. It will be useful for studying any process on DNA when approximation to the natural conditions is desired. Moreover, it will be necessary for the other ongoing project in our laboratory on tumor suppressor p53, and will help to provide preliminary data to support a DOE or NIH proposal for the

investigation of the role of p53 covalent modifications in gene regulation.

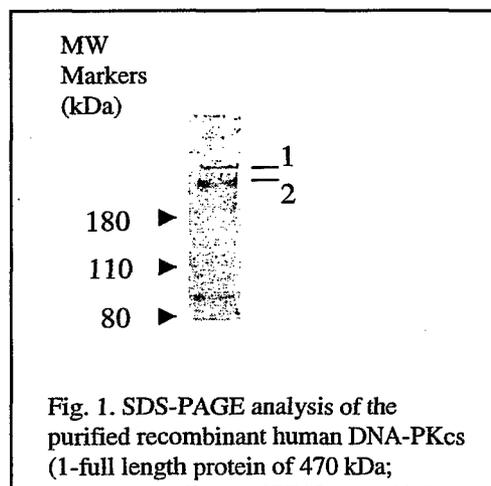
3. To study the mechanisms of NHEJ repair in the context of chromatin, we will have to design and establish a novel experimental system. All presently available *in vitro* models are based on free DNA. However *in vivo*, DNA does not exist as a free species. In a cell, DNA is wrapped around histone octamers and forms a structure called chromatin - an actual substrate for both damage and repair. Chromatin is compact and largely inaccessible for protein binding. It can be unraveled and become accessible only by the action of specific chromatin remodeling complexes. How NHEJ repair proteins gain access to the site of damage in chromatin and which remodeling complexes are involved is not known and cannot be investigated without having a chromatin-based DNA repair model. Establishing this model is the most challenging part of this project. When this task is accomplished, we will have a unique tool for investigating DSB repair at the most advanced level, which will provide a strong basis for NIH grant applications.

TECHNICAL PROGRESS AND RESULTS:

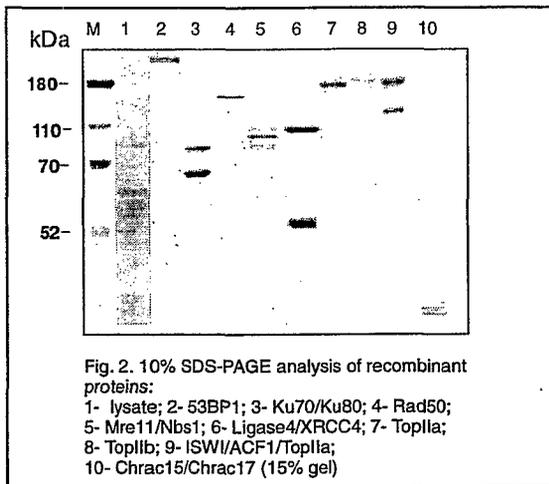
In FY 2002, the major preparative work, the most labor-intensive and time-consuming part of the project, was performed. We (1) constructed protein expression vectors; (2) established a baculoviral protein expression system that allows obtaining large eukaryotic proteins in the insect cells for functional and structural studies; (3) cloned, sequenced, expressed in the insect cells, and purified the proteins needed to reconstitute the NHEJ complex and the chromatin assembly system (Part 1 of this proposal).

In FY 2003, our effort was directed toward: (1) completion of protein expression and purification; (2) reconstitution of recombinant sub-complexes of NHEJ machinery by co-expression and of purified components; (3) reconstitution of functional recombinant chromatin remodeling complex by co-expression; (4) development of human recombinant chromatin assembly system; (5) cloning, expression, purification, and functional analysis of the additional components found necessary for the project (Part 1 and 2 of this proposal).

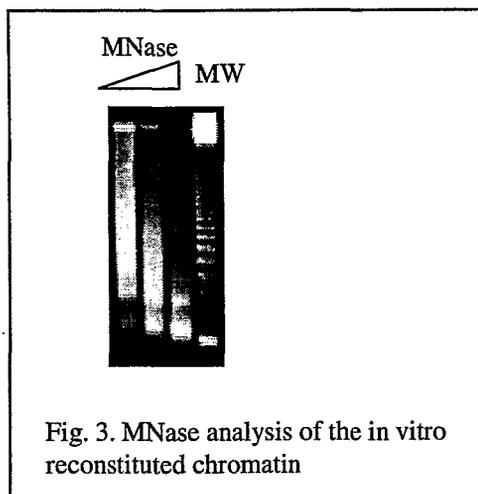
- We expressed and partially purified human DNA-PKcs (470 kDa), the largest protein so far expressed in the insect cells (Fig. 1).



- We reconstituted human Ku70/Ku80, Rad50/Mre11/Nbs1, and LigaseIV/XRCC4 complexes (Fig. 2).
- We reconstituted human chromatin remodeling ACF complex of recombinant ACF1, ISWI-2H, ISWI-2L, Chrac15, and Chrac17 (Fig. 2).



- We developed a human chromatin assembly system composed of recombinant ACF complex, purified histone proteins H2A, H2B, H3, and H4 and DNA purified by CsCl equilibrium centrifugation (Fig. 3).



- Through an optimization of *in vitro* chromatin assembly system, we demonstrated the requirements for the additional components, namely Topoisomerase II alpha and/or beta (170 and 180 kDa respectively) and histone chaperone Nap1 (40 kDa). They were cloned, sequenced, expressed in the insect cells, and purified by the affinity chromatography (Fig. 2). Functional competence of the purified proteins was

characterized by DNA-relaxation assay (for Topoisomerases) and by increased deposition of histone H2A/H2B dimer in the chromatin assembly reactions (for Nap1).

- We found that addition of these components to the chromatin assembly system improved its performance.
- We cloned, expressed and purified human 53BP1 (250 kDa) protein of unknown function associated with NHEJ and interacting with DNA repair proteins (Fig. 2). We designed a functional test, which allowed us to assess 53BP1 function in relation to chromatin. Our preliminary results indicate that 53BP1 may provide an important link between DNA repair factors and chromatin remodeling by facilitating histone acetylation by chromatin modifying enzyme p300.

SPECIFIC ACCOMPLISHMENTS:

This project was presented to the BNL scientific community through the Goldhaber Distinguished Fellows First Annual Presentations on October 23, 2002, and to the Site Visit by DOE Program Managers held in the Biology Department on January 9, 2003. The completed part of the proposal was used as preliminary results for the NIH R01 grant application with J. Hainfeld, Principal Investigator. The grant was funded for the period of 2003-2008.

LDRD FUNDING:

| | |
|---------|----------|
| FY 2002 | \$63,659 |
| FY 2003 | \$61,070 |

Creating a MicroMRI Facility for Research and Development

Helene Benveniste

02-008

PURPOSE:

The goal of this project is to establish a joint high-field, high-resolution magnetic resonance imaging (microMRI) laboratory at Brookhaven National Laboratory (BNL) and the University of Stony Brook (USB). The microMRI laboratory will serve as a research facility for several federally funded BNL and USB investigators whose research requires functional and high-resolution anatomical imaging of small animals and/or plants. A small-bore (20-cm) high field MR instrument dedicated to imaging is currently unavailable at BNL and USB. The microMRI instrument will add great value to the current imaging infrastructure at BNL. The 9.4T MicroMRI instrument arrived in September 2003 and is in the process of being commissioned.

APPROACH:

The scientific interest in high resolution imaging technology suitable to image small animals such as mice has escalated over the last few years as a consequence of the increase in genetically engineered mouse models of human disease. This LDRD project has enabled the establishment of an Magnetic Resonance Microscopy (MRM) facility at BNL, but more importantly it has fostered scientific collaborations between investigators at BNL and outside universities during the establishment of the facility. Below we describe the ongoing projects.

TECHNICAL PROGRESS AND RESULTS:

Project 1: Morphological Characterization of Neuroanatomy in Transgenic Dopamine-2, Dopamine-4 Receptor mice and Dopamine Transporter Gene deficient mice using Magnetic Resonance Microscopy

Collaborators: S. Blackband (UFL), S. Grant (UFL), P. Hof (Mt. Sinai), Yu Ma (Mt. Sinai/BNL), Peter Thanos

In collaboration with Drs. Blackband and Grant at the Center for Structural Biology, University of Florida, we have acquired high resolution T2*- and diffusion-weighted MRM images of D2 -/- (knockout) and age-matched wildtype controls (D2 +/+). Figure C.9 shows representative diffusion-weighted MRM images of a 10-month-old control D2(+/+) mouse (left) and age-matched Dopamine receptor-2 (D2) knockout mouse D2(-/-) (right) and acquired at the 17.1T MR instrument at UFL. The spatial resolution of the MRM images is 52 x 52 x 52 micron-cube.

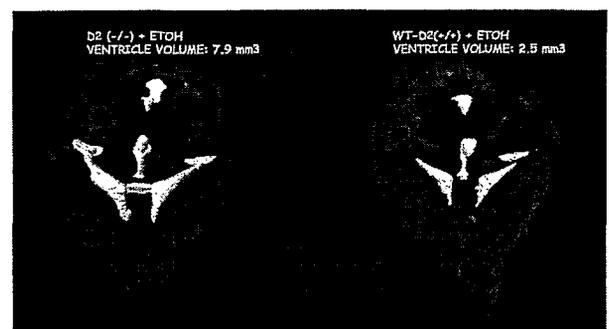


Figure: 3D volume rendered MRM data sets (left=knockout, heterozygous, right=Wildtype, homozygous). The CSF filled ventricular spaces were highlighted in color using Amira software. It is clear that the D2 knockout mouse brain (left) exhibits larger ventricles compared to the D2 heterozygous mouse brain (right) following alcohol exposure. These preliminary data suggest that the D2 receptor can modulate ETOH-induced toxicity.

Project 2: Develop a Computational Infrastructure to archive, query, extract, analyze, and disseminate MR imaging data of DA transgenic mice.

Collaborators: Aditya Siram, SUNY-SB, Y. Ma (BNL), H. Gupta (SUNY-SB)

Database. We are in the process of building a relational database to store large amounts of data generated as part of our projects. In particular, for our overall morphological analysis and hypothesis testing of transgenic mice, we need to build a relational model so that we can archive, display, analyze, query, and disseminate the MR microscopy data of the D2, D4 and DAT transgenic mice. Moreover, to enable data analysis and data sharing (e-collaboration) among researchers at USB and BNL, we will make our database available online through many web-based querying tools as described below. Since most archiving and query utilities are already available within a database management system, we would need to only develop certain software modules such as data format conversion module for DICOM (digital image communication in medicine) standard.

Project 3: Anatomical Semi-Automated segmentation of MRM images acquired from C57BL6/J mouse brains.

Collaborators: Yu Ma (Mount Sinai), Patrick Hof (Mount Sinai), Aditya Siram, SUNY-SB, A. Toga (UCLA)

We are in the process of developing 'gold-standard' anatomical templates based on T2*-weighted MRM images acquired at high field. The objective is to implement these templates in semi-automated segmentation algorithms.

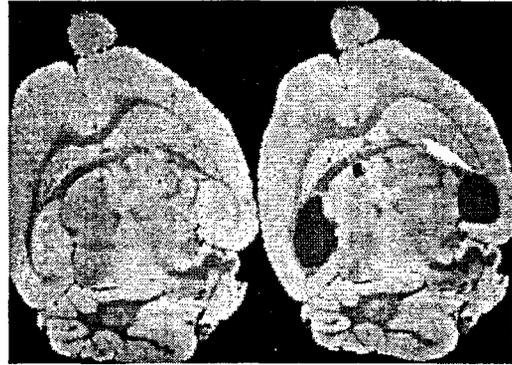


Figure: T2*-weighted MRM images acquired at the 17T at University of Florida. In collaboration with anatomists and computer scientists at UCLA and BNL, we have developed semi-automated segmentation algorithms to accurately label anatomical regions of interest.

SPECIFIC ACCOMPLISHMENTS:

Publications:

17.6 MR Microscopy of the C57BL6/J Mouse Brain: Verification of MR-defined Hippocampal Anatomical Structures. L. Zang, S. C. Grant, A. Siram, P. R. Hof, S. J. Blackband, and H. Benveniste. *J. Neuroscience* (in press)

Du, C.; Pan, Y.T.; MacGowan, G.A.; Koretsky, A.P.; "Separation of Calcium Transients and Motion Artifact using Frequency Filtering of Fluorescent Signals Arising from the Perfused Mouse Heart," *Proceedings of Society of Optical Engineering (SPIE)*, in "Functional Monitoring and Drug-Tissue Interaction," Vol. 4623, pp281-286

Du, C.; Pan, Y. T.; MacGowan, G.A.; Koretsky, A. P.; "Decreasing Motion Artifacts in Calcium-Dependent Fluorescence Transients from the Perfused Mouse Heart using Frequency Filtering," *Cell Calcium*, in press

Pan, Y. T.; Xie, T. Q.; Du, C.; Bastacky, S.; Meyers, S.; Zeidel, M. L.; "Enhancing Early Bladder Cancer Detection with

Fluorescence-guided Endoscopic Optical Coherence Tomography," *Optics Letters*, in press (2003)

Presentations:

MRI Safety: International Society for Magnetic Resonance in Medicine, Section for Magnetic Resonance Technologists, May 10-16, Toronto, Canada

Meetings:

Du, C.; MacGowan, G. A.; Benveniste, H.; Koretsky, A. P.; "Optical Optimization in

Calcium Transient Detection from Intact Mouse Heart," 2003 Biomedical Engineering Society Annual Meeting, October 1-4, Nashville, TN

Benveniste, H.; Du, C.; "Multimodality Imaging," Neuroimaging Workshop of DOE, October 19, Boston

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$ 94,494 |
| FY 2003 | \$193,613 |
| FY 2004 (budgeted) | \$180,000 |

Targeting Tin-117m to Estrogen Receptors for Breast Cancer Therapy

Kathryn Kolsky

02-009

PURPOSE:

Most malignant tumors express one or more receptor proteins that are absent or subdued in normal cells. Targeting such exclusive proteins with radionuclides to image or treat tumors is a very attractive approach. The targeting moiety most often is an analog of the natural ligand for the receptors. In this project we propose to synthesize Sn-117m labeled precursors that will selectively bind to the estrogen receptor on malignant breast carcinoma, while sparing the surrounding normal tissue. A majority of breast cancer cells express high levels of estrogen receptors that could be targeted for radiotherapy using short-range β^- or other electron emitters. Sn-117m emits abundant low-energy, high linear energy transfer (LET), monoenergetic conversion electrons that are lethal within a range of 200-300 nm from the site of localization. No significant efforts to label estrogen receptor ligands with radiometals have been made, despite some success that has been demonstrated using In-111-labeled octreotide that targets somatostatin receptors on neuroendocrine and a few other tumors. Radiohalogens, such as Br-80m or I-125 have been used for targeting estrogen receptors in very limited studies, but the results were only mildly encouraging. Radiometals promise prolonged residence time in the tumor by virtue of their slow metabolic efflux, and thus estrogens labeled with Sn-117m are expected to have better therapeutic efficacy than I-125 or Br-80m in terms of tumoricidal index.

APPROACH:

We propose to synthesize 11-methoxy-16-alpha estradiol and radiolabeled it to either I-123 or I-124. The I-124 radiolabeled compound would be used to study the time dependence of occupancy of brain estrogen receptors by anti-cancer drugs like Tamoxifen. This compound would also be radiolabeled with C-11 in a separately funded project to study the same occupancy rate but on a shorter time frame given the greatly reduced half-life of C-11 compared to I-124. The I-123 labeled compound would be tested for efficacy for estrogen receptor targeted therapy of breast cancer in xenografted nude tumor mice.

TECHNICAL PROGRESS AND RESULTS:

A research associate was hired to synthesize the required ligand molecules and started to work on the project in July 2002. During FY 2003 he attempted to synthesize a candidate molecule (No. 4 in Figure 1) which would be subsequently radiolabeled with Sn-117m. He completed approximately 80% of the synthesis, but the final steps were proving more difficult than anticipated (preparing compound No. 5).

However, several developments have occurred which forced us to abandon this molecule. This first problem to arise was the anticipated unavailability of any no-carrier-added radioactive tin, whether Sn-113 (for initial studies) or Sn-117m. The one remaining commercial vendor for Sn-113 has ceased distribution of this isotope. The Sn-117m was to be provided by a separate grant, but production is not planned until FY 2005 beyond the time scope for this project. Another development arose upon more careful consideration of the cell killing ability of Sn-117m. Based on the known maximum density of estrogen receptors

found in tumor cells, the specific activity of Sn-117m, and hence the number of possible Auger electrons, and the pharmacokinetics of estrogen receptor ligands, we concluded that the number of Auger electrons emitted by Sn-117m probably would not achieve a significant cell kill, though this would have been verified by us with experimental data had the radioisotope been available.

At this time that we began to talk with a new scientist in the Medical Department, Anat Biegon, and we discussed whether we could collaborate on a project to develop a steroid hormone radioligand that could be labeled with PET isotopes for her Pet brain studies and with I-123 for the Auger studies initially proposed for this project. The advantages to this collaboration are several. The new research associate could take advantage of a diverse group of mentors, organic chemists, Zizhong Li and Yu-Shin Du, within the PET group of the Chemistry Department, and nuclear and radiolabeling chemists, myself and Dr. Biegon of the Medical Department. The synthesis of proposed molecule, 11-

beta-methoxy-16-alpha-iodo-17-beta-estradiol, would not be difficult since the synthesis of analogues has already been developed by colleagues of Dr. Biegon's.

We also investigated the availability of the iodine isotopes required, I-123 and I-124. I-123 is commercially available from several vendors. Iodine-124 would initially be obtained from a colleague at Memorial Sloan Kettering Cancer Institute. Eventually if larger quantities are required, we would produce I-124 on-site using the Chemistry Department cyclotron.

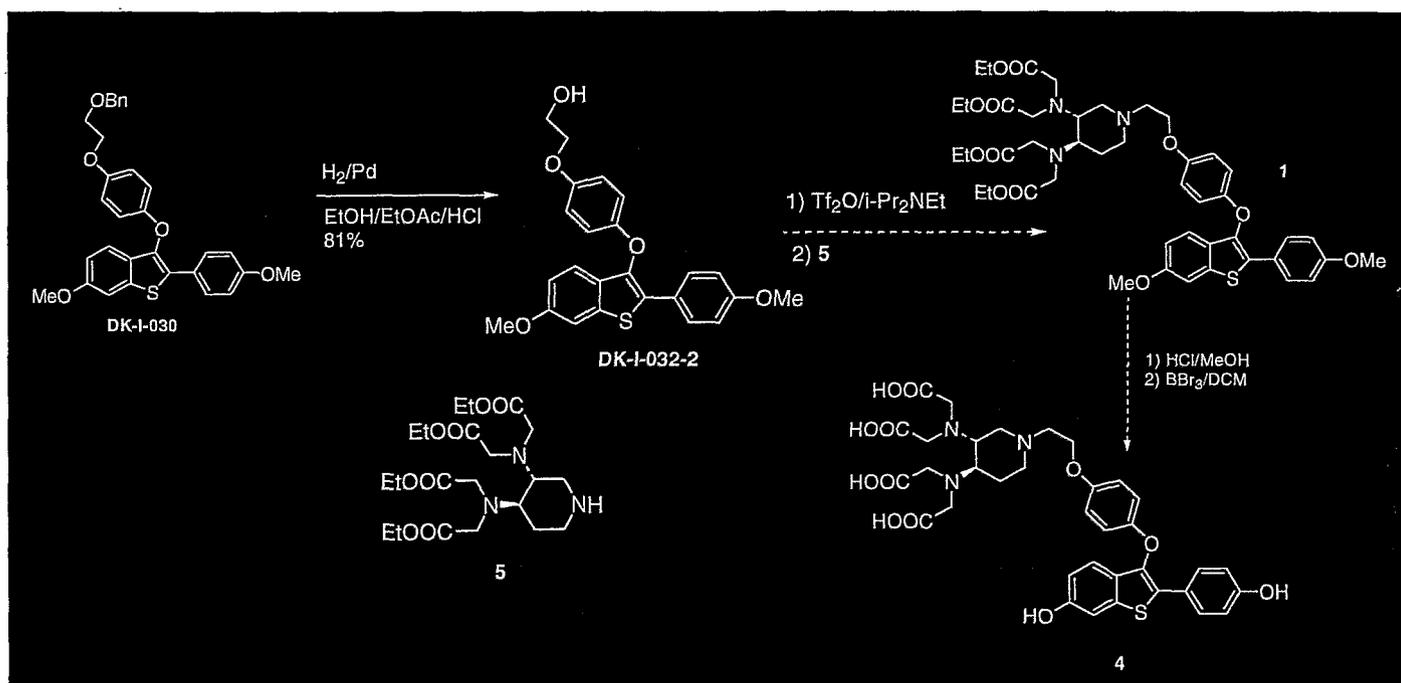
SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2002 | \$48,242 |
| FY 2003 | \$98,671 |
| FY 2004 (budgeted) | \$50,000 |

Figure 1. Synthetic work accomplished during FY 2003 (up to synthesis of compound No. 1). Work on synthesizing compound No. 5 was continuing until Dmitry Kosynkin, the research associate, left the project.



Biom mineralization of Actinides: A Mechanistic Study of the Genesis of Novel and Stable Compounds

Arokinsamy J. Francis

02-016

*G. Vazquez
C. J. Dodge
J. B. Gillow*

PURPOSE:

Elucidate the fundamental mechanisms of stabilization of soluble actinides (organic- and inorganic-complexes and colloidal forms) by naturally occurring phosphate and polyphosphate-producing microorganisms. To specifically investigate (i) the nature of association of U with phosphate, polyphosphate (PolyP), and various phosphate minerals, and (ii) the influence of uranium in phosphate metabolism and complexation of U by the bacteria.

Relevance. Results of this basic research should lead to (i) a better understanding of the environmental conditions likely to foster retardation of actinide mobility and transport, and (ii) strategies for engineered long-term immobilization of actinides in waste repositories, and in contaminated soils, sediments, and wastes.

APPROACH:

In this study, we intend to (i) elucidate the fundamental mechanisms of stabilization of soluble uranyl ion by naturally occurring phosphate and polyphosphate-producing bacteria *Halomonas* sp., (ii) Characterize the nature of the association of actinides with the polyphosphate mineral; (iii) evaluate the stability of uranium with newly formed polyphosphate mineral phases at different pHs; and (iv) establish the kinetics of

phosphate metabolism for the model microorganism and (v) determine the effect of the actinide addition on phosphate metabolism in *Halomonas* sp.

Uranyl nitrate is to be used as a model compound. *Halomonas* sp was selected as the PolyP producing model organism for detailed metabolic study. Speciation and molecular association of uranium with polyphosphate will be determined using spectroscopic techniques. We will use long chain polyphosphate standards containing 10 - 20 phosphate units.

TECHNICAL PROGRESS AND RESULTS:

Analysis of polyphosphate-uranium complex: Polyphosphates are linear polymers of tetrahedral orthophosphate units linked through common oxygen atoms by phosphoanhydride bonds. They have numerous and varied biological functions, among them are its chelating properties. We investigated the complexation between polyphosphate and uranium at different pHs by potentiometric titration, elemental analysis of supernatant and precipitate, and EXAFS.

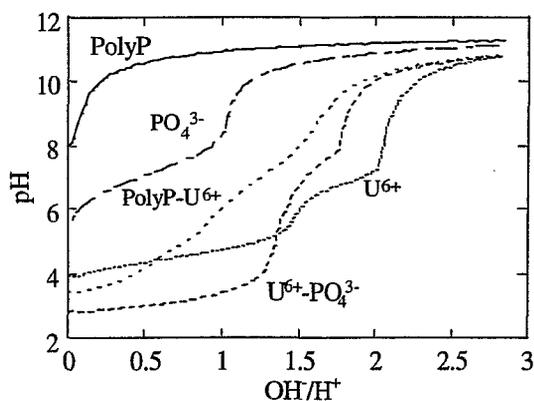


Figure 1 Potentiometric titration of uranium, phosphate, uranium phosphate, and uranium polyP associated with phosphate and polyP.

Comparison of the potentiometric titration curves for U-PolyP, U^{6+} , and PO_4^{3-} (Fig. 1) shows two sharp inflection points at 1.4 and 1.8 mmOH⁻/mmH⁺ for the U-phosphate, while the U-Poly-P sample exhibited two broad inflection points at 1.0 and 1.5 mmOH⁻/mmH⁺. This suggests differences in the extent of uranium complexation for each ligand.

The PolyP- U^{6+} complex formed at pH 3, 4.5, and 6.0 showed a slower rate of precipitation for U-PolyP complex compared to the immediate precipitation of U-phosphate. The PolyP- U^{6+} complex precipitate contained varying P:U ratios as a function of pH, with a higher ratio at low pH indicating a greater "selectivity" of the PolyP for uranium at lower pH. Preliminary analysis of the raw EXAFS data of U association with PO_4^{3-} and PolyP formed at pH 3, 4.5, and 6.0 shows there is an increase in the presence of mixed-phases such as uranium hydroxophosphato and uranium hydroxide species as a function of increase in the pH (Fig 2).

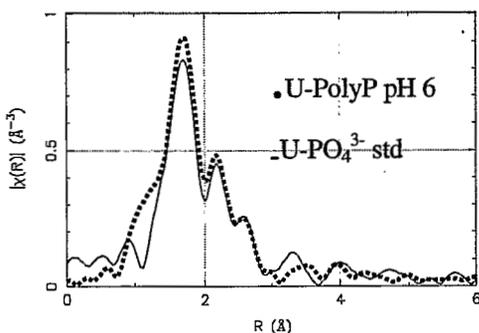


Figure 2. Fourier transformed EXAFS spectra at the U L_3 edge showing U association with phosphate standard and with polyphosphate.

These results suggest that the mechanism of complexation between uranium and PolyP is different than uranium and phosphate; the reaction kinetics is slower and the precipitate goes through an initial colloidal phase.

Phosphate accumulation pattern in *Halomonas* sp grown under aerobic and denitrifying (anaerobic) conditions. The accumulation kinetics of phosphate by *Halomonas* sp. grown under aerobic conditions showed that it is accumulated during the initial lag phase, and reaches a maximum of 0.22 g/g dry wt. of cells. It decreases during the exponential growth phase and reaches 0.02 g/g dry wt. of cells at the stationary phase (Fig 3).

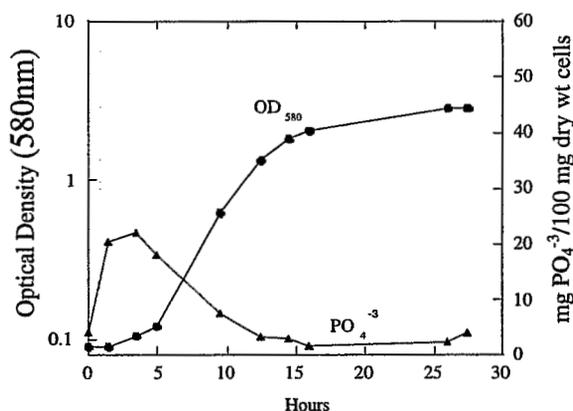


Figure 3. Kinetic of phosphate accumulation in *Halomonas* sp under aerobic growth conditions.

Halomonas sp. grown under denitrifying (anaerobic) conditions shows a similar pattern of phosphate accumulation. Phosphate is accumulated during the early exponential phase (0.20 g/g dry wt. of cells) and decreases to 0.02 g/g dry wt. of cells at the stationary phase (Fig 4).

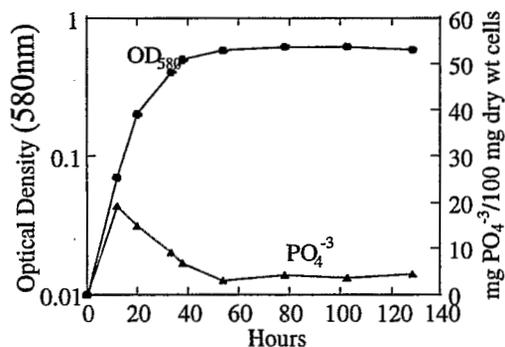


Figure 4 Kinetic of phosphate metabolism in *Halomonas* sp grown under denitrifying conditions.

Effect of uranium on PolyP accumulation:

The influence of addition of the uranium on phosphate metabolism in *Halomonas* sp cells is shown in Fig 5. After 30 min. and 90 min. incubation of the cells with the actinide, the phosphate concentration decreased to 58 % and 79 % respectively, while the control sample containing no uranium showed only 7 % and 19 % decrease in the phosphate concentration for the indicated times (Fig 5). In these studies all the added uranium was removed from the solution during the first 30 minutes of incubation (data not shown). The analysis of the biomass showed 0.2 g U/ g dry wt. of cells. This suggests that U is sequestered by cellular phosphate or U inhibits the metabolism and release of phosphate. Fundamental understanding of the nature of association of uranium with phosphate minerals and their interactions with microorganisms at the molecular and biochemical level will be useful in the

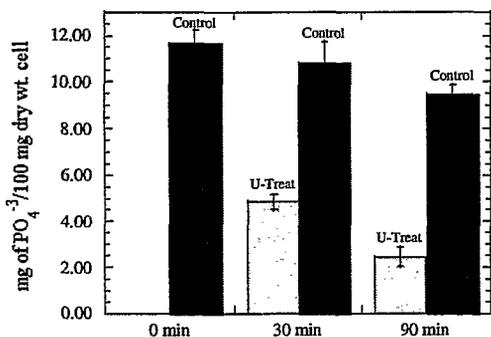


Figure 5. Effect of addition of uranyl nitrate (35mM) on phosphate metabolism in cells of *Halomonas* sp.

selection of appropriate microorganisms for the biogenesis of phosphate containing mineral phases and the long-term immobilization of actinides and toxic metals. Future work will involve extension

of these studies to other actinides and toxic metals.

SPECIFIC ACCOMPLISHMENTS:

Francis, A. J.; Gillow, J. B.; Dodge, C. J.; Harris, R.; Beveridge, T. J.; Papenguth, H. W. Association of Uranium with Halophilic and Non-halophilic Bacteria and Archaea. (*Manuscript submitted to Radiochim. Acta*).

Manuscripts in preparation.

Vazquez, G. and Francis, A. J. Modulation of Poly(3-hydroxybutyrate) (PHB) and Polyphosphate (polyP) metabolism in *Halomonas* sp.

Vazquez, G.; Dodge, C. J.; and Francis, A. J. Interaction of Polyphosphate with Uranium under Different pH Conditions.

Presentations

Vazquez, G.; Dodge, C. J.; and Francis, A. J. Uranium Complexation with Polyphosphates, Paper presented at the 226th American Chemistry Society National Meeting, September, 7-11, 2003 New York.

Vazquez, G.; Dodge, C. J.; and Francis, A. J. Uranium Interaction with Bacterial Phosphates. Presented at the Center for Environmental Molecular Science (CEMS) Annual Meeting at the Stony Brook University, May 22, 2003, New York.

LDRD FUNDING:

| | |
|---------|----------|
| FY 2002 | \$88,871 |
| FY 2003 | \$92,482 |

Using Mini-LIDAR for Verification and Long-term Monitoring of Cover Systems

John Heiser

02-017

PURPOSE:

The Environmental Research and Technology Division (ERTD) at BNL developed a novel methodology for verifying and monitoring caps and cover systems (covers) used to remediate hazardous and/or radioactive waste sites. The technology uses gaseous perfluorocarbon tracers (PFTs) to determine the flaws (e.g. holes or cracks) and high permeability areas in the system. This project developed a Light Detection and Ranging (LIDAR) system that can be used to detect PFTs in the air and will replace the traditional soil-gas sampling and gas-chromatographic analysis of the PFT(s).

Long-term monitoring and verification of covers is of great interest to The Department of Energy – Environmental Management (DOE-EM). With the increased focus on accelerated clean up at the various DOE sites, there is considerable concern about long-term stewardship issues in general, and verification and long-term monitoring (LTM) of covers, in particular. DOE-EM set up a national committee of experts to develop a long-term capping guidance document. The Principal Investigator (PI) for this project was on the committee and served as the verification/LTM expert. This LDRD focuses on developing a new and novel detection technology. Once developed, the technology would also be useful for monitoring and surveying for contaminants such as volatile organic compounds (VOCs). We will leverage the LDRD in an attempt to secure new funding in the area of LTM and will also pursue

funding for in-situ real-time monitoring of VOCs in such areas as dynamic underground stripping of VOCs from groundwater. [PFTs are VOCs and success in detecting PFTs will lay the groundwork for detection of VOCs as they pertain to DOE remediation and technology requirements.]

APPROACH:

The BNL cover verification/monitoring technology uses gaseous tracers, which are injected below a cover and searched for above the cover. The sampling grid, concentration and time of arrival of the tracer(s), are used to determine the size and location of flaws and to determine relative permeability of the barrier.

Traditionally, detection of the PFTs has been done using gas chromatography. This method requires gas-sampling ports placed on 5 to 10 foot spacing throughout the barrier and air sampling equipment to draw the samples to the gas chromatograph (GC). Installation of the ports is time consuming and requires penetrations into the ground. Any penetrations into the ground, even if they do not penetrate the cover itself, introduce additional potential failure points. Sampling a typical one-acre site with 5 foot spacing would also require 800 sampling ports. GC analysis of this many ports is time consuming and can be very expensive (currently ~\$135 per sample).

BNL collaborator, Art Sedlacek, has considerable experience with laser systems and in particular LIDAR. Mini-LIDAR systems appear to be ideally suited to the detection/monitoring needs of PFTs in the application of cover system verification and monitoring. Literature suggested that for PFTs, detection limits as low as 0.1 ppb may be achievable. A Mini-LIDAR system could be set up at a cover system and the laser used to scan the entire field. The system would simultaneously measure

concentrations and locations of PFTs above the cover system. This information would be translated to assess the performance of covers in a manner similar to using conventional GC analysis.

TECHNICAL PROGRESS AND RESULTS:

During FY 2002, a tunable, CO₂ laser was refurbished and brought into operating condition. A laboratory-based, bench top LIDAR was configured. The system schematic is depicted in Figure 1 and the laboratory set-up is pictured in Figure 2.

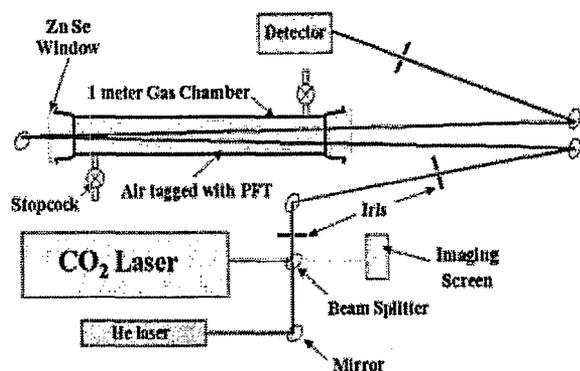


Figure 1. Schematic of laboratory test set-up for PFTs

The absorption cross-section obtained from a plot of peak height versus concentration, gave a value of $3 \times 10^{-18} \text{ cm}^2$, which was the same order of magnitude compared to literature values for similar perfluorocarbon compounds. These laboratory experiments achieved a resolution of approximately 10 ppb-m.

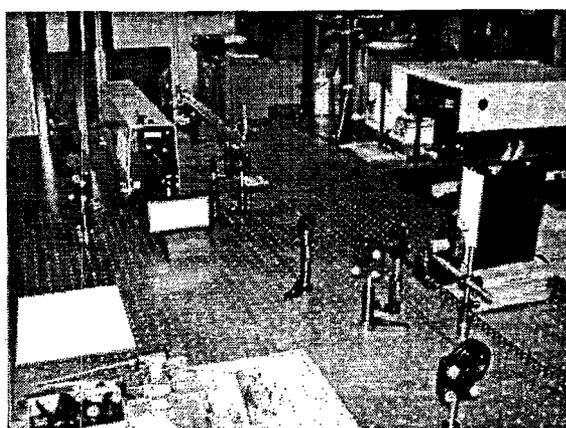


Figure 2. Photograph of laboratory set-up (with laser path appended).

In FY 2003, Fourier-Transform Infrared (FTIR) spectra for Perfluoromethylcyclohexane (PMCH) were measured to make certain that we were not missing a more desirable absorption line. Figure 3 depicts the FTIR spectra from 950 to 1050 wavenumbers. Two adsorption maxima exist which correspond to the R(20) and P(40) laser lines. The R(20) line was the line used for the laboratory measurements, thus confirming that we were working in the optimal lasing region. A HgCdTe detector (Judson Series J15D) was purchased that was more specific to this region and had a larger surface area. It was believed the 10 ppb detection limits would be improved using the new detector.

The LIDAR was reconfigured from a laboratory (sealed cell) fixed path length system to a field deployable variable path length system. A narrow hallway approximately 50 meters in length was chosen for the measurements. The CO₂ laser was positioned such that the laser light was directed into the hallway. A 10:1 ZnSe (99.2 % transmission @ 10.6 μm) beam expander and collimating telescope was used to minimize beam divergence and enlarge the spot size to approximately 25 mm. A mirror and reflector were used to direct the beam down the 40-meter hallway and back to the detector.

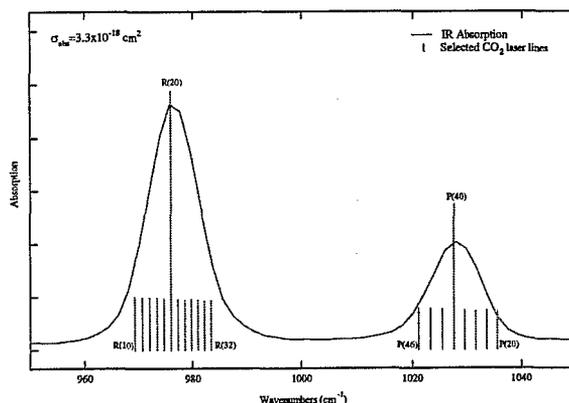


Figure 3. FTIR for the perfluorocarbon tracer PMCH

With the new detector, the baseline output proved to be two orders of magnitude greater than the first detector. A preliminary check of the LIDAR was completed by releasing PMCH into the hallway from a cylinder. As expected, the signal from the LIDAR decreased with time as the tracer concentrations in the hallway rose. Figure 4 shows the detector voltage versus time (chopped signal) for LIDAR measurements made during the tracer release (solid lines) and subsequent decay after the cylinder was closed (dashed lines). The baseline (no tracer) is represented by the top two curves. While the tracer concentration was not measured, this test was a quick check of the LIDAR's response to PFTs in the air and was very promising.

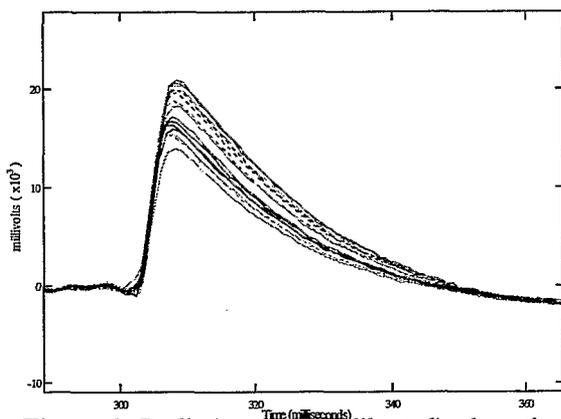


Figure 4. Preliminary (not calibrated) adsorption curves for PMCH in air

The next step was to tag the hallway air with a known or measurable amount of PMCH. The LIDAR returned to the zero tracer state rapidly in the first test and suggested a high air exchange rate in the hallway. A tracer test was performed to measure the air exchange rate of the hallway. The calculated exchange rate was used to determine the release rate for PMCH to obtain a concentration of 240 ppt in the hallway.

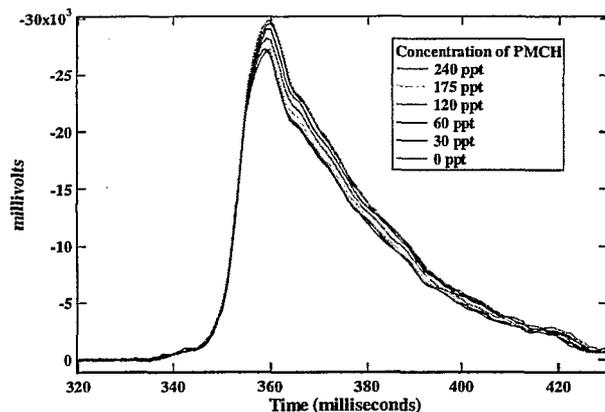


Figure 5. Adsorption curves for PMCH in air

The hallway air was tagged (using constant release rate, permeation sources) with PMCH and allowed to equilibrate over night. The LIDAR was then turned on and measurements taken. The LIDAR was left on and the PMCH sources were removed from the hallway. This allowed the PMCH to decay away. Since the hallway air exchange rate was known, the decay rate was also known and data from the LIDAR was taken every two minutes as the tracer depleted from the hallway atmosphere. Figure 5 shows the adsorption traces taken from PMCH = 240 ppt until a stable unchanging baseline occurred (PMCH below detection levels). We were able to detect PMCH in the air at levels as low as 30ppt. This corresponds to 1 ppb-m and is a ten-fold increase in sensitivity versus the FY 02 laboratory results.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$124,610 |
| FY 2003 | \$124,084 |

Electrical Systems Reliability

Robert A. Bari

02-022

PURPOSE:

To develop a methodology for a probabilistic assessment of the security of electrical energy distribution networks including the future grid system which relies heavily on the communication industry for monitoring and protection. The identification of potential failure modes and their likelihood will inform decisions on potential modifications to the network including hardware, monitoring instrumentation, and protection systems. We will extend the technology developed and apply the techniques to address the electrical configuration of the Con Edison system. We have been working collaboratively with Con Edison in this area. The Long Island Power Authority (LIPA) has expressed its interest in collaborative projects with BNL in this area. Successful achievement of this research by developing and demonstrating the methods could establish BNL as a frontier laboratory in the areas of reliability assessment of electrical power grids.

APPROACH:

The traditional approach to electrical grid reliability is based on deterministic analyses for congestion and transient response under normal conditions or a condition that satisfies "a single failure criterion." Such methods have shown to be effective and have resulted in sound designs, which are robust to major single failures. Past events have shown that multiple cascading failures under unfavorable conditions have been the major contributor to losses of electrical distribution systems. The Northeast blackout of August 14, 2003, is a recent dramatic example of this behavior. Another factor in

the evolution of the electrical grid system is their ever-increasing reliance on communication infrastructures for protection and monitoring which are not easily amenable to traditional deterministic analysis.

Powerful reliability methods have been developed in the past three decades in the nuclear industry, which could be tailored for use in evaluating the reliability of the existing and the future electrical grid system. These methods have the capability of systematically and in an efficient manner, incorporating the deterministic models for congestion and transient response analyses.

Others have developed methods for identification of the potential vulnerability of a large grid system using the grid topology (e.g. application of small world techniques), and use of empirical fault propagation using epidemiological models. These methods are macroscopic in nature and do not address the detailed design issues of a grid system. At best they can identify portions of the grid that are suspected of potential vulnerabilities.

In contrast to these models, our model is microscopic in nature and relies heavily on the specific design of the portion of the grid being analyzed. It extensively models the types of faults the grid could potentially experience, the response of the grid, and the specific design of the protection schemes. The importance of fault detection and protection schemes is heavily emphasized and the role of future reliance on the communication infrastructure is addressed. Finally, the methods proposed are quantitative in nature, thereby allowing prioritization, reliability allocation to different modules, and the verification of the design that meets the allocated reliability goal.

A time-dependent computer simulation model with sufficient flexibility to analyze a range of security problems will be developed. Once the model is established and challenges are prioritized, we will develop potential strategies and activities to address these challenges. The strategies may consist of network design improvements, hardware redesign, improvements or additions to monitoring capabilities, software redesign, and operating procedure revisions.

TECHNICAL PROGRESS AND RESULTS:

We conducted a pilot study and utilized the methodologies from probabilistic risk assessment for the first time. The objective of the study was to use the methodology and a sample application, to come up with an initial estimate of the order of magnitude contribution of the communications network to the electrical grid reliability, as well as contribution of other major components. We used a hypothetical electrical network design based on a portion of the grid in New York City, owned and operated by Consolidated Edison Company of New York, as the example for demonstrating our approach. The study clearly showed and demonstrated that the PRA technology can be utilized for reliability assessment of the electrical grid system. It was shown that the probabilistic risk assessment (PRA) technology used in this manner is microscopic in nature and relies heavily on the specific design of the portion of the grid being analyzed. It extensively models the types of faults that a grid could potentially experience, the response of the grid, and the specific design of the protection schemes.

An integrated power system simulation software EPTOOL, which is capable of analyzing power flow, small signal dynamics, and transient dynamics, has been successfully developed. Power system components are modeled extensively in this package. A distinctive feature, which is highly applicable to the proposed probabilistic reliability evaluation approach of this software, is the precise modeling of impacts of protection devices on the system stability after a large disturbance. Various power system protection devices and strategies are implemented to investigate the realistic events that may occur to power grids according to the adopted protection features that can be combined easily in the simulation study. The software can be used to evaluate the coordination between power system protection and control to provide quantitative backup analysis of the proposed reliability evaluation approach.

SPECIFIC ACCOMPLISHMENTS:

A draft report was issued in FY 2003. Con Ed is reviewing this material to assure that confidentiality is not violated. A paper will be submitted to an appropriate refereed journal in FY 2004. A presentation of results to DOE was made in December 2003. A proposal has been sent to DOE's new Office of Transmission Reliability on an assessment of the restoration process for the blackout of August 14, 2003.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$ 83,965 |
| FY 2003 | \$ 99,081 |
| FY 2004 (budgeted) | \$104,000 |

Liquid Fuel Gasifier for Combustion and Fuel Cells

Thomas Butcher

02-024

PURPOSE:

Liquid fuels provide high energy densities and this provides a great advantage particularly for remote or mobile applications. In many applications however, a gaseous fuel offers critical advantages in emissions, heat transfer, and flame control. Conversion of oil to gaseous fuels in practical systems can be complicated by coke and deposit fouling. The purpose of this project is to develop oil-to-gas conversion methods via vaporization and partial oxidation which can lead to ultra-low NOX oil combustors and oil reformers for fuel cells.

APPROACH:

A major problem which has been encountered in prior related work is successful vaporization and partial oxidation of oil without the formation of soot, deposits, and coke. This depends on the chemical structure of the fuel, and on the process in the vaporizer/partial oxidizer. Conventional vaporizers have separate feed of air and atomized fuel to the processing zone. Our group has developed a low pressure air atomization concept in burner applications, where the fuel spray and air are nearly premixed in the nozzle and a flame with a high internal recirculation rate. This patented concept is now being used in several other burner development projects. In this project we are exploring the deployment of this concept for a liquid fuel, partial oxidation gas generator.

Following vaporization, oxidation of the fuel under "cool flame" conditions is being

studied as a method of generating a fuel gas which will not recondense on downstream surfaces. These cool flame reactions occur between 320 and 400 C and have been studied in some detail with model compounds (n-heptane). Some results in the literature have shown that these reactions can be used with practical fuels, such as diesel oil, followed by porous surface burners. There is, however, no available data on the products of the low temperature oxidation step with practical fuels. This is needed to allow system design optimization, extension to other conditions, and comparison with other technical options which do not include this step.

Planned work in this area includes a detailed review of prior work followed by a design of a facility at BNL which will enable the study of these reactions with a practical fuel, using the BNL air atomization concept.

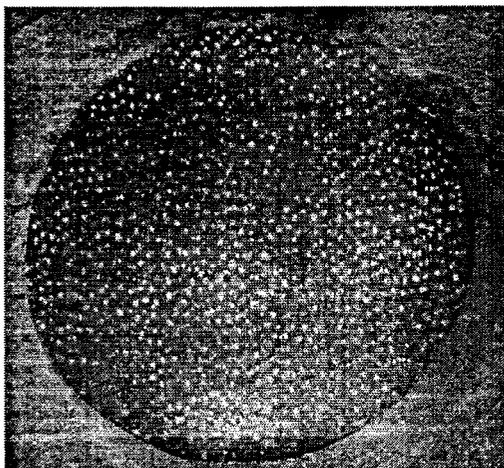
Project collaborators at BNL include Dr. C.R. Krishna, Dr. Abdallah Naidja (FY 2002) and Dr. Devinder Mahajan.

TECHNICAL PROGRESS AND RESULTS:

A detailed review of the prior literature in this area was completed in FY 2002. From this the key issues to be evaluated have been identified as well as a preliminary reaction model. The results of this detailed review have been compiled in a review paper. Following from the review a test reactor, air heater, and atomizer concept were designed and built. FY 2003 experimental work was completed using this equipment, which provided a stable, repeatable platform for studies of cool flames with liquid fuels. Measured reactor temperature rise and oxygen consumption was found to be in good agreement with literature values. Analysis of the recondensed fuel species showed nearly complete conversion to polar

compounds including alcohols, aldehydes, ketones, etc.

A controlled temperature probe was inserted into the cool flame product gas to quantify the rate of recondensation of products as a function of probe temperature. The recondensation was not found to be much different than would be expected for simply vaporized fuel and this has very important implications for the design of burners or reactors which use the cool flame process. Essentially the cool flame products must be kept hot to avoid deposition and subsequent coke deposit formation.



Some exploratory studies were done in which the products of the cool flame were burned within a ceramic matrix. Results showed good combustion with ultralow emissions of NOx – under 10 ppm.

SPECIFIC ACCOMPLISHMENTS:

Oxidation of Fuels in the Cool Flame Regime for Combustion and Reforming for Fuel Cells, Naidja, A.; Krishna, C. R.; Butcher, T.; and Mahajan, D.; Progress in Energy and Combustion Science, Vol. 29, No. 2, pp. 155-191 BNL 69349 2003.

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$ 72,993 |
| FY 2003 | \$109,000 |

Study of a Power Source for Nanodevices

Mow S. Lin

02-031

PURPOSE:

It is possible to build nanodevices out of nanowires, tubes or other blocks. However, to power such devices on a nanoscale is challenging. A naturally occurring powerhouse will be used to prove the concept. The natural powerhouse built as part of the nanodevice will be driven by solar energy, converting photo-energy into electric potential, thus avoiding transmission of power via direct wiring. The molecular power supply is bacteriorhodopsin (BR), a purple-colored membrane protein isolated from the bacterium *H. halobium*, which displays outstanding stability and non-linear optical properties. The object of the work is the integration of the photo-driven proton pump (BR) with functional groups in nanodevices in order to overcome power transmission problems inherent to such devices (especially free-moving ones). This work could lead to the development of a process of fabricating nano-electronics, ultra-fast photoactive on-off switches, biosensors, and solar energy converters.

APPROACH:

The self-assembly on silicon surfaces has been systematically studied on a variety of pure and doped silicon crystals. The first emphasis was to arrange the BR molecule at specific positions on silicon surfaces. Other molecules for example, fullerenes, porphyrins, conjugated polyenes, and thiophenes have also been considered as candidate backups with different self-assembly techniques.

Langmuir-Blodgett (LB) techniques were used for assembly of molecules, either by evaporating a thin monolayer film of the molecule or by dip-and-pull from a monolayer film formed in the trough. This step allows for spontaneous assembly on silicon Si (100) surface templates. Then molecules with specific properties (e.g. conduction, charge transfer or fluorescence quenching moiety) can be attached in conjugation with specific properties of BR. The synthesized molecules of nanometer size can be recovered from the template and characterized. Molecules with special properties can be used as building blocks or subject to further reactions for building complex materials.

Different templates: Si(100) surface templates have been studied for their sensitivity to pH and surface modification agents in an attempt to alter the template for different synthesis. Other surfaces e.g. Si (111), semiconductor, GaAs, ITO and other metal oxides were planned for testing as templates.

Field and medium effects: The synthesis has been carried out under magnetic and electric fields in an attempt to change the orientation of the absorbed molecules on the template.

Critical-state control: for setting up two systems adjacent to phase transition or defects such that the synthesis can be conducted along the interfaces in controlled orientation.

TECHNICAL PROGRESS AND RESULTS:

In FY 2002, all required equipment and materials were obtained. The bacterium *H. halobium* was cultured and its membrane protein bacteriorhodopsin was isolated and purified to the highest quality. The monomeric protein unit was extracted from

the membrane with a Triton X-100 detergent and purified by dialysis out of the detergent. It was compressed into a monolayer film in the LB trough. The self-assembly experiment was performed to spread a monolayer of bacteriorhodopsin units on a silicone wafer. Structure determination using Atomic Force Microscopy (AFM) in the STEM group in the BNL Biology Department showed good progress. Most recent work has focused on the assembly of molecules with specific properties (e.g. conducting wires or tubes) over the bR film.

SPECIFIC ACCOMPLISHMENTS:

The Principal Investigator was Program Chair for the "2nd Annual Emerging Information Technology Conference (EITC)" and organized a session on nanotechnology which relates to the work of this program.

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$ 99,920 |
| FY 2003 | \$100,000 |

Ultrafast Nonlinear Spectroscopic Studies of Model Catalytic Surfaces

Nicholas Camillone III

02-042

PURPOSE:

The objective of this LDRD was the design, construction, and development of instruments and methods for nonlinear optical probing of the chemistry of surfaces in ultrahigh vacuum, atmospheric pressure, and liquid ambients. The instruments and expertise developed are positioned to make contributions in areas of significance to chemical physics, catalysis, and nanoscience.

APPROACH:

Over the last decade, second harmonic generation (SHG) and sum frequency generation (SFG) have been demonstrated as powerful, non-invasive probes of interface structure, reaction kinetics and adsorbate dynamics. Advances in the control of interface structure at the nanoscale by physical, chemical, and electrochemical methods paralleled this work. Recently Somorjai and Freund and Rupprechter have demonstrated the potential of combining nonlinear optical techniques and nanomaterials for identifying adsorption sites, determining differences in adsorbates on supported nanoparticles as compared to single crystal surfaces and directly comparing the nature of adsorbates on model catalysts at high pressure (~ 1 atm) to those in ultrahigh vacuum. Thus, the convergence of nanomaterials preparation and nonlinear spectroscopic technologies has opened new possibilities for probing surface chemistry.

In such studies ultrashort (~ ps) pulsed lasers (pulse energies ~ 1 $\mu\text{J}/\text{cm}^2$) generate high electric field strengths at low average powers, giving rise to nonlinear spectroscopic signals without perturbing the system. At higher pulse energies (~ 1 mJ/cm^2), photons can initiate chemistry. As proposed in follow-on projects, with addition of a pulse amplifier to the system constructed under this LDRD, high-pulse energies will be used to “pump” adsorbate-nanoparticle complexes and various probe techniques will be employed to follow the evolution of photoinitiated chemical events with femtosecond resolution.

Plan to develop the capabilities for optically probing chemical reactions at surfaces involved: installation of the laser; characterization of the laser output; design, construction, and testing of the detection apparatus; design, construction, and testing of three sample vessels — a spectrochemical cell, a UHV chamber, and an atmospheric pressure reaction vessel; and application of the apparatus to the study of adsorption kinetics at the solid-liquid interface.

TECHNICAL PROGRESS AND RESULTS:

In FY 2002, preparation of a new laboratory for Class IV laser operation, including design and installation of a door interlock, was completed. A femtosecond Ti:Sapphire laser system, homebuilt autocorrelator, group velocity dispersion compensator (GVDC), optical components for manipulating the laser light and photon counting apparatus for detecting the second harmonic (SH) signal were installed. Figure 1 shows results of pulse characterization measurements and simulations. The capabilities of the surface SHG system were validated by comparison of measurements of the rotational anisotropy of

SH from the SiO₂/Si(111) interface in air with those found in the literature.

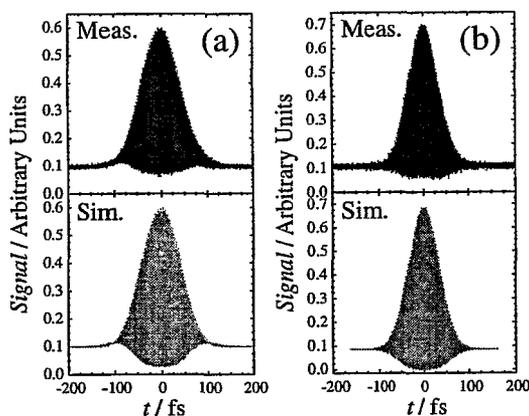


Figure 1. (a) Measured and simulated interferometric autocorrelation patterns indicated an 80 fs pulsewidth and a linear frequency “chirp” of $3 \times 10^{-4} \text{ fs}^{-2}$ before the GVDC and (b) a 52 fs pulsewidth with no indications of a frequency “chirp” after the GVDC.

Apparatus for SHG measurements of surface reaction kinetics in a liquid environment were designed, constructed, and applied to the study of self-assembled monolayer growth kinetics. The setup consisted of a sample mount, a spectrochemical cell, a reservoir and two peristaltic liquid pumps. Solvent is circulated through the system by the pumps, and the reservoir allows for nitrogen bubbling, mixing, filtering and the abrupt introduction of solutions to the sample while maintaining a low level of turbulence in the cell. Measurements of the flow rate dependence of the adsorption kinetics of decanethiol on Au(111) surfaces were made (Figure 2). These measurements are the first demonstrating a systematic dependence of adsorption rate on flow rate for self-assembling amphiphiles from solution.

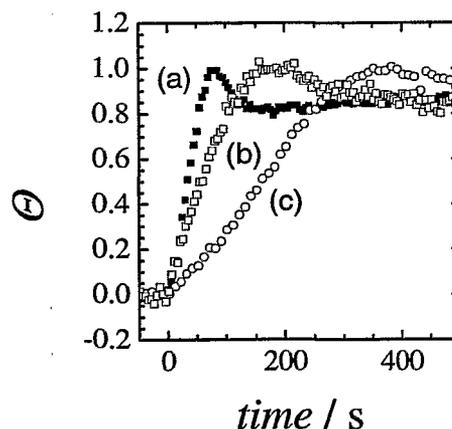


Figure 2. Thiol uptake curves measured *in situ* during self-assembly of decanethiol on Au(111) in 2 μM solution at flow rates of (a) 1.0, (b) 0.22 and (c) 0.1 mL s^{-1} showing an increasing rate of adsorption with an increasing solution flow rate.

During FY 2003, data from these experiments were interpreted as demonstrating the limiting role of solute diffusion in the self-assembly process. When a fluid flows past a surface under laminar flow conditions, the velocity of the flowing fluid approaches zero with increasing proximity to the surface, and can be thought of as forming a boundary layer of a thickness that is inversely proportional to the square root of the stream velocity. Within this layer, we expect some degree of depletion despite mass transport due to the flow. The depth of the depletion, or “diffusion layer,” can be estimated from

$$\delta = D^{1/3} \nu^{1/6} \sqrt{\frac{x}{U}}$$

Where D is the diffusion coefficient for the solute, ν is the kinematic viscosity of the solvent ($0.014 \text{ cm}^2 \text{ s}^{-1}$), x is the distance from the edge of the sample surface to its center measured along the direction of the flow and U is the mean stream velocity, which is estimated from the measured flow rate and the volume of the solution in the cell. A plot of the growth rate vs. δ reveals a linear relation (Fig. 3) as expected assuming that outside the diffusion layer the

concentration approaches that of the bulk solution. Thus, the flux to the surface which, by Fick's first law is proportional to the concentration gradient, is a linear function of the width of the diffusion layer. This agreement supports the conclusion that transport through the diffusion barrier limits the growth rate at the relatively low concentration employed in these experiments ($2 \mu\text{M}$).

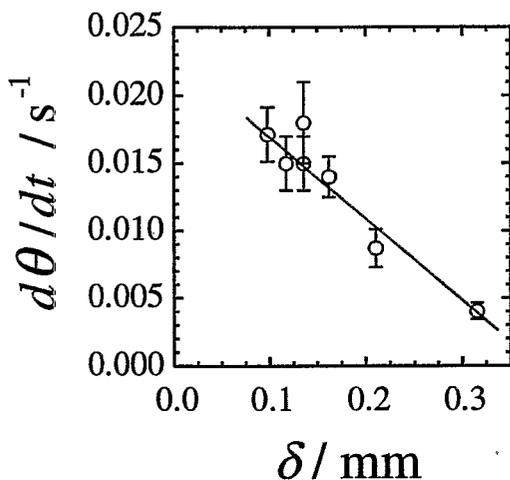


Figure 3. Initial monolayer growth rate plotted vs. estimated diffusion layer depth. The data are well-fit by a straight line. See text for further explanation.

Construction of the UHV surface analysis system with attached atmospheric-pressure reaction chamber was completed. The features of the multi-level chamber illustrated in Fig. 4 include: temperature programmed desorption (TPD) spectrometry, low-energy electron diffraction (LEED), a cylindrical mirror energy analyzer (CMA) for Auger electron spectroscopy, an x - y - z - θ UHV crystal manipulator, a retractable effusive beam gas doser and multiple windows for laser access on both the UHV and atmospheric pressure levels. The differentially-pumped atmospheric pressure cell is suspended below the UHV chamber and is designed for quick sample exchange without necessitating the exposure of the UHV region to atmosphere.

During the summer of 2003, Ted Pak, a high school student, worked in the lab as part of this project to interface the quadrupole mass spectrometer (QMS) and the crystal manipulator heating system to a computer for making TPD measurements. This involved writing temperature control and data acquisition software. In addition, he began work on TPD spectra simulation software that can be used to quantify adsorbate-surface and adsorbate-adsorbate interactions based on measured TPD data.

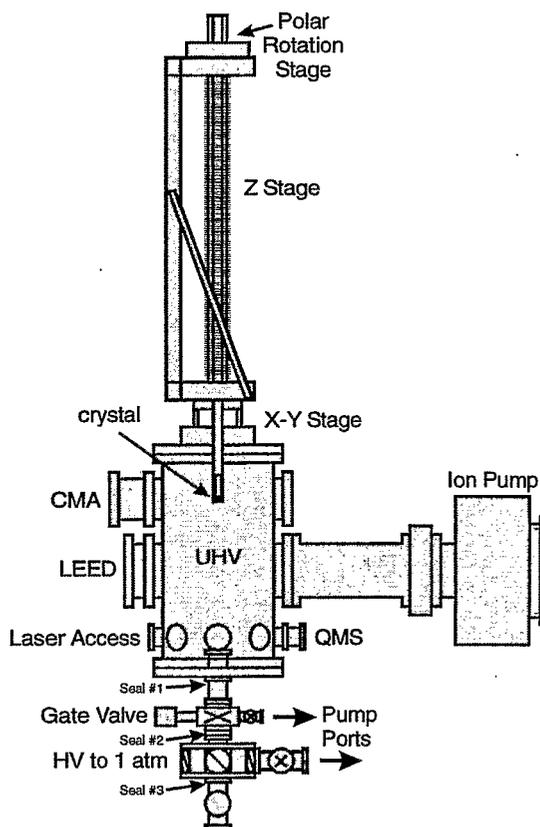


Figure 4. Schematic illustration of the UHV surface preparation and analysis chamber and the attached atmospheric pressure reaction cell.

SPECIFIC ACCOMPLISHMENTS:

Formal Proposals:

- Camillone was Co-Principal Investigator in a proposal submitted January, 2001, in response to the DOE Office of BES *Nanoscale Science, Engineering and Technology* solicitation for DOE lab

activities. The proposal was entitled: "Preparation and Characterization of Metal and Alloy Nanoparticle Electrocatalysts." Co-Principal Investigators: J. McBreen, R. Adžić, and S. S. Wong. This proposal was not funded.

- Camillone was Co-Principal Investigator in a portion of the Brookhaven Center for Functional Nanomaterials Jumpstart Program, submitted November, 2002, for the "Ultrafast Optical Sources Cluster." Co-Principal Investigators: B. Sheehy and A. Cook. No funding for Camillone was granted.

- Camillone was a Contributing Collaborator in a proposal submitted in March, 2003, in response to the DOE Office of BES *Catalysis Science* solicitation. The proposal was entitled: "Understanding and Manipulating the Active Site in Catalytic Reactions." Lead Principal Investigator: J. Hrbek. This proposal was not funded.

- Camillone was Co-Principal Investigator in a new LDRD submitted April, 2003, entitled: "Biolipid Metal Nanocrystal Superlattices: A Nanobiotechnology Project." Co-Principal Investigator: J. Hainfeld. This proposal was not funded.

- Camillone was Principal Investigator in an LDRD submitted April, 2003, entitled: "Femtosecond Photoinitiated Nanoparticle Surface Chemistry." Collaborators: A. Harris and J. Misewich. Projected Funding: \$121,000, FY 2004 and 2005.

- Camillone was Principal Investigator in a proposal to the DOE Office of BES entitled "Ultrafast Investigations of Surface Chemical Dynamics." Co-Principal Investigators: A. Harris and M. White. Funding: pending, FY 2005 through 2007.

LDRD-Related Presentations:

- "Photons & surfaces: manipulating and monitoring reaction pathways," N.

Camillone III, presented at the *Friday Society*, (BNL Chem. Dept., October 11, 2002).

- "Non-linear spectroscopic probes of the molecular dynamics at the active site," N. Camillone III, presented at a *Catalysis Initiative Planning Session* (BNL Chem. Dept., December 19, 2002).

- "Ultrafast nonlinear spectroscopic studies of model catalytic surfaces," N. Camillone III, presented at the *Mid-Year Review of LDRD Projects* (BNL, April 1, 2003).

- "Exploring the dynamical roots of reactivity at localized nanostructures," N. Camillone III, presented at the *Workshop on Reactivity at Localized Nanostructures* (BNL Chem. Dept., July 16, 2003).

- "Ultrafast Investigations of Surface Chemical Dynamics," N. Camillone III, presented at the DOE Chemical Sciences Review (BNL Chem. Dept., October 28, 2003 — FY 2004 activity linked to FY 2003 proposal submission).

Publications:

- Manuscript submitted to *Langmuir*, (2003): N. Camillone III, "Diffusion-limited thiol adsorption on the gold (111) surface."

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$184,847 |
| FY 2003 | \$185,000 |

Combined Use of Radiotracers and Positron Emission Imaging in Understanding the Integrated Response of Plants to Environmental Stress

Richard A. Ferrieri
M. Thorpe

02-045

PURPOSE:

A long-standing challenge to plant biologists has been to obtain a sound understanding of the physiological basis for whole plant responses to environmental conditions. While plants have evolved complex mechanisms that coordinate the distribution of nutrients between foliage and roots with well-balanced water gradients throughout the vascular architecture, the identification of these important mechanisms and their interaction with the rhizosphere under altered environmental conditions has proven to be elusive, particularly as it requires observing the growth processes within intact plants where tight feedback controls operate. Very little information exists on the interrelationship of these processes largely because of the lack of *non-invasive* techniques to observe them within intact plants. The purpose of this project is to develop appropriate tools using nuclear imaging that will allow us to measure spatial and temporal profiles of radioactivity within intact plants and address fundamental questions linking plant responses through allocation of C, N and water to certain environmental conditions.

APPROACH:

We use short-lived positron emitting radioisotopes including ^{11}C (half-life, 20.4

min), ^{13}N (half-life, 9.97 min) and ^{15}O (half-life, 2.04 min) which provides two benefits in plant research when compared with more traditional approaches using longer-lived radioisotopes such as ^{14}C or tritium, or with using stable isotopes such as ^{13}C , ^{15}N or ^{18}O . Firstly, these isotopes decay by emission of very energetic positron (β^+) particles that annihilate yielding coincident gamma rays. Thus, it is possible to spatially and temporally resolve plant nutrient-water fluxes *non-invasively*. Secondly, the short half-lives eliminate buildup of radioactivity in the organism and surrounding rhizosphere thus allowing for multiple administrations of tracer over time. This aspect is key to providing a holistic understanding that better correlates response to a set of conditions.

TECHNICAL PROGRESS AND RESULTS:

Presently, we have developed capabilities to administer ^{11}C to plants as carbon dioxide, ^{13}N as nitrate or ammonium, and ^{15}O as water all within a brief period of time. The diversity here is made possible owing to the Facility's Ebco TR-19 and JSW 41" cyclotrons that can operate in unison for isotope production. The Facility's ^{11}C platform (Figure 1) utilizes a unique rapid pulse-labeling approach while implementing full environmental controls for maintaining photosynthetic capacity while gaining feedback on tracer fixation, transpiration rates, atmospheric emissions including respiration (Figure 2) and volatile organic compounds (VOCs) (Figure 3), and mobile sugar fluxes within the plant (Figure 4).

Additionally, we've established methods for administering ^{13}N and ^{15}O using a split root compartment to allow measurements of root uptake and whole-plant allocation of mineralized N sources and water fluxes.

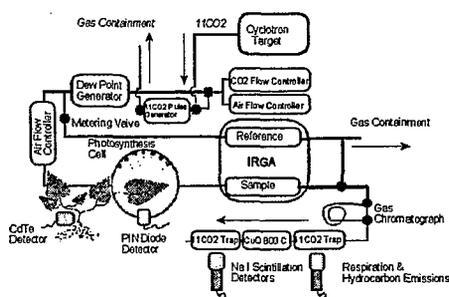


Figure 1. Schematic drawing of ^{11}C platform.

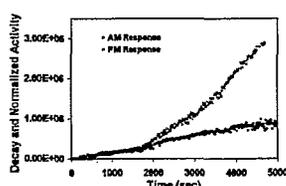


Figure 2. Diurnal effects on $^{11}\text{CO}_2$ respiration in *Populus tremuloides*. Note higher respiration rate later in the day.

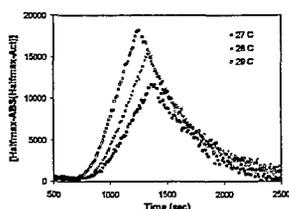


Figure 3. The ability to measure temporal profiles of tracer flux through the hydrocarbon pathways can provide a *non-invasive* approach for assessing enzyme activity.

Using Positron Emission Tomography (PET) and Positron Radiography, it is possible to image and quantify nutrient allocation patterns and temporal fluxes of materials across scales of the entire plant including above (Figure 4) and below ground (Figure 5).

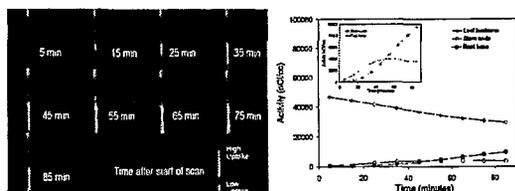


Figure 4. PET images of spring wheat (*Triticum aestivum*) 10 min after administration of $^{11}\text{CO}_2$. PET enables us to acquire whole-plant data on radio-labeled sugar fluxes.

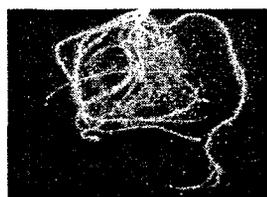


Figure 5. Positron image of spring wheat (*Triticum aestivum*) root area provides information on spatial allocation between active root zones and meristem.



Figure 6. Positron image of paper birch seedling (*Betula papyrifera*) showing above ground allocation of $^{13}\text{NO}_3^{-1}$ 30 min after lateral administration of tracer.

Recent work has focused on investigating links between plant responses to water stress and responses to insect herbivory. The underlying hypothesis is that plant defensive responses, whether to climatic or herbivory actions, may be generalizable. We are in the early stages of exploring impacts of water stress on plant carbon management. Figures 6 and 7 show an example of short-term responses to water stress in paper birch seedlings (*Betula papyrifera*) on net respiration.

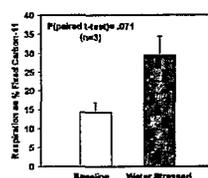


Figure 7. Plant respiration as measured by ^{11}C emission in *Betula papyrifera* increased two-fold after one week of water stress.

These changes correlate with net decreases in photosynthetic capacity, as well as with decreases in the transpiration stream. Preliminary results also suggest there are

increases in phloem sugar fluxes which may link to reallocation of starch-sugar pools.

We've recently completed a study linking effects of defense inducement using the induction signal compound, jasmonic acid (JA), on carbon allocation. Recent evidence suggests that herbivory can induce changes in carbon allocation within a leaf, and may possibly affect whole plant resources. $^{11}\text{CO}_2$ was administered locally and systemically to *Populus tremuloides* and *Populus nigra* clones in combination with JA treatments (Figure 8).

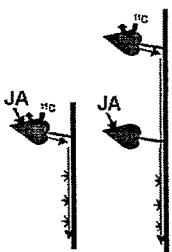


Figure 8. Schematic showing area where the tracer was administered in relation to JA treatments. Control treatments followed the same procedure using a similar treatment spray, but lacking JA.

Sugar fluxes and allocation were measured using a combination of imaging approaches described and nuclear counting techniques. Results 6 hrs after JA treatment showed an increase in ^{11}C sugar fluxes both locally (Figure 9) and systemically (Figure 10) with noted generalized trends of increased basipetal-to-acropetal allocation. The temporal changes in carbon allocation and export after treatment were consistent with the senescence onset promoting effects that past reports have attributed to JA. Data also showed that JA treatment elevated ^{11}C isoprene emissions with no change in tracer specific activity. This data suggests that JA induces a rapid shift in allocation of recently fixed carbon, shunting carbon away from temporary starch storage in the leaf, and into other pathways such as production of isoprene and mobile sugars.

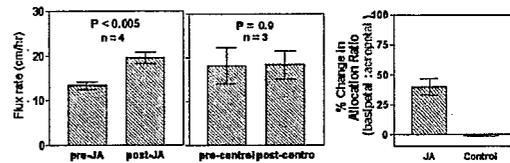


Figure 9. Local flux rates for ^{11}C sugar transport in JA treated and control treated aspen (*Populus tremuloides*). Image data showed increased basipetal allocation.

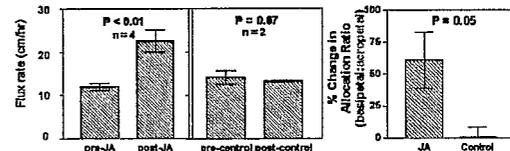


Figure 10. Systemic flux rates for ^{11}C sugar transport in JA treated and control treated hybrid poplar (*Populus nigra*). Image data showed similar increased basipetal allocation.

SPECIFIC ACCOMPLISHMENTS:

Patent application filed: "Rapid Impulse Feeding of $^{11}\text{CO}_2$ to Plants with Real-time Positron Imaging."

Manuscript submission: "Rapid Pulse Labeling of Plants with Carbon-11 Combined with Imaging to Assess Carbon Allocation." *Plant, Cell & Environment*.

Manuscript in preparation: "Measuring Rapid Changes in Carbon Transport and Allocation in *Populus* in Response to Jasmonic Acid using Carbon-11." *Plant, Cell & Environment*.

Paper Presented (B. Babst, Tufts U. collaborator): *Phloem Conference, Bayreith, Germany*, "Measuring Rapid Changes in Carbon Transport and Allocation in *Populus* in Response to Jasmonic Acid using Carbon-11."

NSF FIBR pre-proposal submitted: "Roots, Water, and the Rhizosphere:

Flushing out a New Paradigm for Below Ground Biology.”

USDA proposal in preparation: “Water Stress Effects on Soybean-rhizosphere Relationships Linking C, N Allocation.”

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$ 99,220 |
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$150,000 |

Arranging Nanoparticles into Arbitrary Patterns with Optical Trapping

Christopher Fockenber

02-046

J. P. Kirby

T. J. Sears

PURPOSE:

We proposed to build an apparatus, which combines optical trapping (laser tweezers) and self-assembly to form two-dimensional structures of metallic (*e.g.*: gold) nanoparticles. Optical trapping is used to hold nanoparticles at key positions in the desired structure followed by “filling in” of the gaps exploiting attractive and/or repulsive interaction among the nanoparticles established by suitable molecules adsorbed on their surfaces. The objective of this work is to determine the feasibility of our idea. In this respect, synthesizing capping molecules for, and trapping of, gold nanoparticles as well as creating multiple optical traps are the technical challenges of this experiment.

If the molecular links between the metal particles could be made to function as molecular wires, these structures could be operated as practical electronic circuits. Therefore, this work could potentially be incorporated into the Nanoscience Application program of the BNL Nanocenter. Optical traps can also be used as a new tool to study surface chemistry in the liquid phase of single particles using Raman spectroscopy as analytical technique. This could have implications for research of nanocatalysts.

APPROACH:

In contrast to the “top-down” methods used in traditional microfabrication, today’s

nanoscience favors self-assembly as the tool in an indirect construction technique for nanoscale objects. Currently there is quite poor controllability. However, optical trapping (known as “optical tweezers”) has been widely used to manipulate micrometer-sized particles,¹ and extension to the nanoscale is possible. Although optical trapping in the focus of a laser beam applies mainly to dielectric particles, small metallic spheres (diameter $\ll \lambda_{\text{laser}}$) can be trapped in a similar manner.² In addition, multiple traps have been generated by using spatial light modulators creating the desired pattern by way of diffraction.³

Thiols can form highly ordered, self-assembled monolayers at the gold surface by hydrogen bonding (an amidinium-carboxylate salt bridge) among the molecules. Di-, tri-, and tetrathiol compounds were also used to link two or more gold nanoparticles together forming stable dimers, trimers, or tetrahedra. Moreover, gold nanocrystals covered with simple alkanethiols have been shown to arrange in crystal structures (molecular nanocrystals). Instead of using gold-thiol bonds to link two particles, we envision utilizing amidinium-carboxylate salt bridges.

The long-term goal of this project is to combine all of the aspects mentioned above and to create a simple two-dimensional network of metallic nanoparticles.

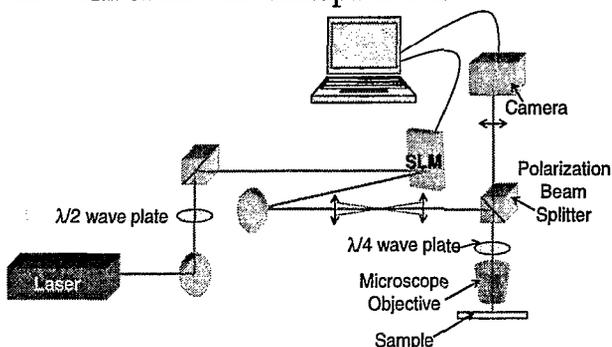


Figure 1. Schematic diagram of the optical tweezers with SLM.

TECHNICAL PROGRESS AND RESULTS:

The basic setup for the laser tweezers has been built including microscope optics and image acquisition.

Trapped particles were observed by imaging the light reflected by the particle onto a CCD camera. Computer programs in LabVIEW™ were written to calculate Fourier images from given phase or amplitude masks. To optimize the masks an iterative genetic algorithm was programmed to adjust the pattern for highest intensity in the focal spots. Based on the results from these calculations, we decided that a phase shifting spatial light modulator (see below) is best suited for this experiment to generate dynamic optical traps.

A preliminary goal of this work was to optimize the experimental conditions so that the time to capture a particle in the trap is minimized, while the retention time in the trap is maximized.

Toward this end, a LabVIEW virtual instrument has been developed to analyze the trapping statistics under different conditions. This algorithm uses basic image processing

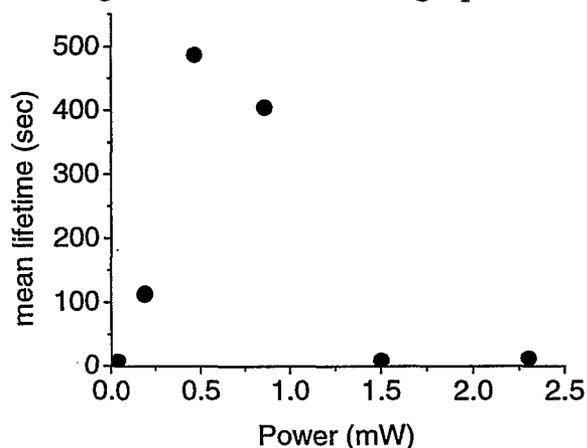


Figure 2. Average retention time of 0.5 μ m latex particles in optical trap as a function of laser power

and blob (threshold) analysis to determine when a particle is present and how long it persists in the trap. These statistics are compiled for several hundred consecutive particles to test the effect of changing the laser power and position.

In an optical trap, the laser power must be high enough to overcome the thermal motions of the particle. However, the competing optical forces that stabilize and destabilize the trap, scale linearly with power, so increasing the power alone cannot improve overall performance. Indeed, high laser power may destabilize the trap by heating the particle, possibly forming vapor bubbles. Large latex (polystyrene) particles (0.5 μ m) are effectively trapped with very low laser power \sim 0.5 to 1 mW (see Fig. 2). Average retention times are 6 to 8 minutes at this power. As laser power increases from 2 to 50 mW, lifetimes fall to an average of 10 to 20 s per particle. The trapping force scales with the size of the nanoparticles, so that higher laser intensities were needed to trap 30 nm particles. Again, trapping was more effective at the lower end of the power range covered (*e.g.* 60 s at 10 mW compared to 16 sec at 40 mW). However, it is more difficult to capture them at low power, as the particles tend to drift past the focus without being retained.

Another goal of this project is the trapping of gold or silver nanoparticles with the green laser. Trapping of gold nanoparticles has been demonstrated under an optical arrangement similar to ours, except in the NIR.^{2,4} In our experiment with 514 nm light, and power ranging from 1 to 100 mW, neither gold nor silver nanoparticles could be trapped for any significant time. The longest retention times for both metals are less than a second. A

possible reason why gold particles behave differently at this wavelength is their larger absorbance in the green. Simple optical force calculations, based on the optics and refraction in and out of the particle, do not directly apply in this or other situations, in which the beam waist, wavelength and particle dimension are all of the same magnitude. However, for particles with dimensions that are smaller than the wavelength of the trapping beam the Rayleigh approximation can be used to estimate the relative trapping forces:^{4,5}

$$F_{trap} = \frac{2\pi nr^3}{c} \left| \frac{m^2 - 1}{m^2 + 2} \right| \nabla(I)$$

$$F_{abs} = \bar{n}_{beam} \frac{8\pi^2 r^3 n^2}{c\lambda} \text{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right) I$$

$$F_{scat} = \bar{n}_{beam} \left(\frac{n}{c} \right) \frac{8}{3} \pi \left(\frac{2\pi}{\lambda} r \right)^4 r^2 \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 I$$

$$I = \frac{n\epsilon_0 c}{2} |\mathbf{E}|^2$$

n is the refractive index of the solvent, m is the generally complex index of refraction of the particle scaled by n ($n_{particle}/n$, see Table 1), r is the particle radius, λ is the wavelength in the medium (λ_{vacuum}/n), \mathbf{E} is the electric field, and \bar{n}_{beam} is the direction of beam propagation.

Table 1: Complex index of refraction

| Compound | λ / nm | $n_{solvent/particle}$ |
|--------------------------|----------------|------------------------|
| Water ⁶ | 514.5 | 1.336 |
| | 1047 | 1.324 |
| Polystyrene ⁷ | 514.5 | 1.600 |
| | 1047 | 1.574 |
| Gold ⁸ | 516.6 | 0.608 + 2.12i |
| | 1033 | 0.272 + 7.07i |
| Silver ⁸ | 516.6 | 0.130 + 3.07i |
| | 1033 | 0.226 + 6.99i |

Making the further assumption that the electric field in the tight focal region of the

microscope objective can be described by Gaussian beam optics, ratios of F_{trap}/F_{abs} and F_{trap}/F_{scat} can be calculated. Under these approximations, the force exerted on the particle by the absorption of green light is indeed responsible for destabilizing the optical trap for gold and surprisingly for silver as well. Contrary to the wavelength used, the gradient force for near infrared light is larger than absorption and scatter forces combined for both metals and trapping is possible as has been observed.

Since F_{abs} is the dominant force for gold particle, we can follow a different strategy similar to the one used for low-index (lower than the solvent) dielectric particles, which are repelled from the laser focus. Low-index particles have been trapped in the dark center of obstructed or donut-shaped beams, or by rapidly scanning the focused laser beam around the particle in a circular motion.⁹⁻¹¹ Such beam shaping can also be accomplished, by using dynamic diffractive optical elements such as a programmable spatial light modulator (SLM).

Recently, we installed a SLM (512x512 NLC, 15 micron pitch, Boulder Nonlinear Systems) in the optical tweezers apparatus. The SLM uses liquid crystal technology to impart a spatially resolved phase pattern onto the reflected laser beam. This phase pattern results in a spatially resolved amplitude pattern (*i.e.* the Fourier transform of the input phase pattern) at the focal spot of the microscope objective. By appropriately choosing the input phase pattern, multiple traps can be independently controlled in the focal plane. In preliminary experiments, up to 4 latex particles (either 0.5 μm or 30 nm diameter) have been trapped simultaneously (see Fig. 3).

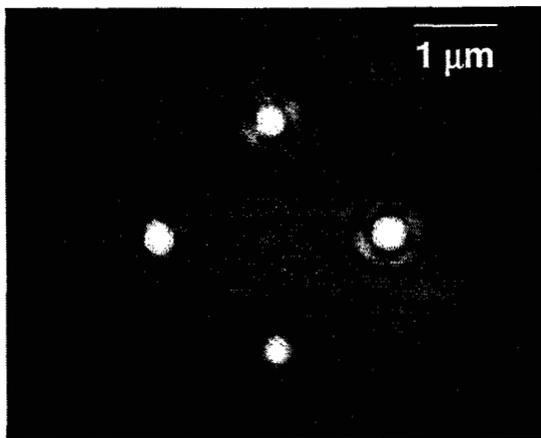


Figure 3. Four polystyrene particles (30 nm diameter) trapped in the optical tweezers. Multiple foci are created by encoding the appropriate phase pattern on the SLM.

The relatively rapid response time of the SLM allows the phase pattern to be updated in real time; thus, single nanoparticles have been “dragged” throughout the focal plane

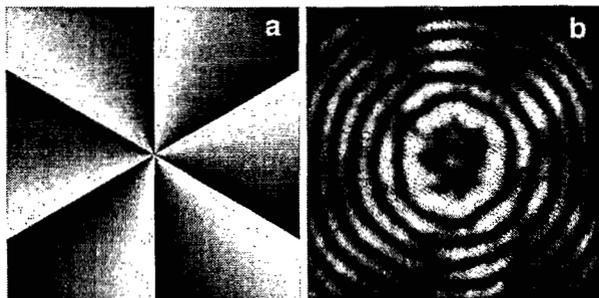


Figure 4. (a) Phase pattern on SLM given by $\phi(x,y)=2\pi x+2\pi y-n \arctan(x/y)$,¹⁰ where n is the pitch of the phase spiral ($n=6$, above). The gray-scale corresponds to phase shifts between 0 (black) and 2π (white), respectively. (b) Resulting light intensity in the tweezers focal plane. Size and position of the donut can be changed by varying the pitch and position of the phase pattern.

using a series of pre-programmed coordinates. In addition, single and multiple “optical donuts” (also known as optical vortices or Laguerre-Gaussian beams) have been created (see Fig. 4). Thus far, we were able to trap multiple dielectric nanoparticles at the bright edges of these rings.

We would like to thank Dr. Laurie M. Yoder for her contribution to this project, in particular setting up the software and hardware for the Spatial Light Modulator.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$119,860 |
| FY 2003 | \$120,000 |

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Advanced Multidimensional Techniques to Explore the Biochemical and Behavioral Consequences of VOC Exposure

Madina R. Gerasimov

02-048

PURPOSE:

Develop the methodology for exposing laboratory animals to precisely measured and controlled levels of volatile organic compounds (VOCs) and to apply this methodology to studying the abuse-related reinforcing and other central nervous system effects of these agents. The technical difficulties of producing strictly controlled exposures to vapors have been limiting the development of the animal model for inhalant abuse. Therefore, this methodology when fully developed sets a stage for exploring the factors contributing to the predisposition, development, and potential treatment of inhalant abuse. We have chosen to utilize the conditioned place preference (CPP) paradigm, a valuable, firmly established, and widely used tool in behavioral pharmacology and addiction research, to measure reward-related behaviors in rats exposed via inhalation to toluene, the essential psychotropic component found in many abused solvents.

APPROACH:

Solvent abuse is a significant worldwide problem associated with serious health and social cost. In addition, a history of inhalant abuse is associated with a substantially increased likelihood of adolescents to develop other substance abuse disorders. Abused solvents are almost always self-administered via inhalation and their very rapid distribution into the brain may result in

immediate reinforcing effects, which contributes to their abuse liability and risk of dependency. Therefore, animal models utilizing the inhalation route are important for studying the abuse-related reinforcing effects of these agents.

Because recovery from toluene exposures is so rapid, there are obvious advantages to conducting training sessions during the inhalation exposure. We examined the rewarding properties of various toluene doses (800-5,000 ppm) in Sprague-Dawley rats using a CPP paradigm with a three-compartment chamber and fully automated computerized recording of the time spent in each chamber during the test session. Because the expression of a CPP can sometimes be greater when animals are tested when under the influence of the training drug, we compared test sessions conducted with and without toluene exposure. In addition, we combined the CPP paradigm with measurements of locomotor activity by recording the number of chamber crossings during the test sessions.

Co-investigators are W. Schiffer and S. Dewey. The expertise of Mr. David Alexoff (bioengineer) and Dr. R. Ferrieri (physical chemist) proved to be invaluable for this project. ERULF student, J. Taibali (Fall Semester 2002), CSI student, Abbi Ferrieri, (summer semester 2002), and an intern from John Jay College of Criminal Justice, Lauren Collier (Fall and Spring 2002/2003), also contributed to this effort.

TECHNICAL PROGRESS AND RESULTS:

We have already achieved the goal of creating and monitoring on-line reproducible levels of toluene within our dynamic exposure animal chambers by using flame ionization detection (SRI Instruments) in

conjunction with gas chromatography (for calibration purposes). These chambers were custom designed and built upon our request by MedAssociates Inc.

- We have performed independent calibration of the FID, and correlated this response with the levels of solvent vapors achieved in the CPP apparatus.

- We demonstrated that our design was truly unbiased, since the rats that received air in both sides (control group) did not show any preference for either the black or white side with approximately equal time spent in either compartment on the test day (Figure 1, left panel). These results for the air control group are very similar to the results for all the test animals when their preference was measured in the pre-conditioning phase (Figure 1, right panel).

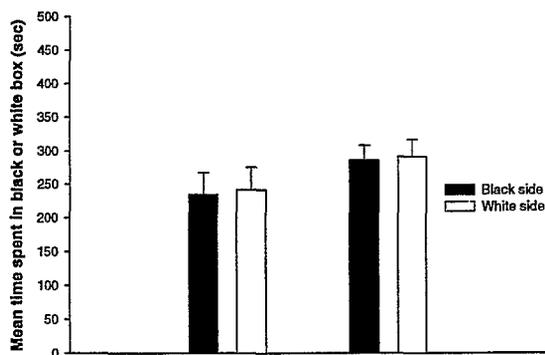


Figure 1. Average time spent in the white or black box of the conditioning apparatus before and after the conditioning phase of the study with air only exposures.

- We established a relationship between the dose of toluene (5000, 2000 and 800 ppm) and the degree of place preference (Figure 2), as well as the effect of the test conditions and the number of training sessions on the outcome measure (time spent in toluene-paired compartment). Animals conditioned with 2,000 and 5,000 ppm of toluene spent significantly ($p < 0.05$) more time on the toluene-paired side than on the air-paired side. Exposure to the training

concentration of 2,000 ppm on the second test day led to the loss of preference for the toluene-paired side in this group of animals.

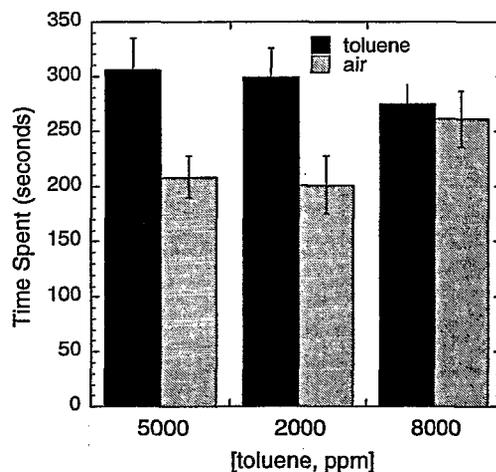


Figure 2. Results of tests for a conditioned place preference with three concentrations of toluene.

- We compared the effects of locomotion inhibitory effects of toluene vapors in toluene-naïve and toluene-trained animals. In the group of animals trained with 2000 ppm of toluene, locomotor activity was significantly ($P < 0.01$) lower when the animals were tested when exposed toluene, as compared to their score obtained during the subsequent toluene-free test session (Figure 3B, left panel). However, no significant difference was observed between toluene-free and toluene-exposed test sessions in the toluene-naïve animals (Figure 3, right panel).

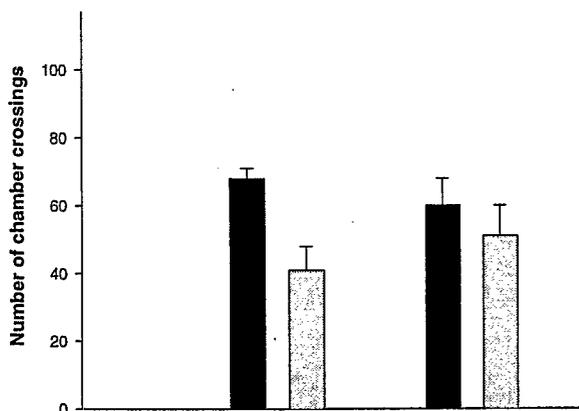


Figure 3. Effects of toluene (2,000 ppm) on locomotor activity during test sessions. Shown are the number of chamber transitions on test day1 (toluene-free) (left panels) and on test day 2 (during exposure to the training concentration of toluene) (right panels) for toluene-trained (black bar) and toluene-naïve rats (grey bar).

In conclusion, we have successfully demonstrated that the CPP paradigm can be used to study abuse-related behaviors of toluene. Because toluene shares many other abuse-related properties with abused solvents, it should be possible to apply this paradigm to the study of other inhalants as well. Toluene's CPP effects were concentration related and occurred in a concentration range consistent with previous behavioral and neurochemical reports. Unlike other drugs of abuse, the expression of toluene CPP was not enhanced by testing during toluene exposure. The CPP model should be very useful for evaluating the abuse potential of various solvents and studying the behavioral and neural bases for their abuse-related effects. Our ultimate goal is to establish a correlation between

behavioral and neurochemical responses to various inhalants and their pharmacokinetic profiles.

This project involves animal vertebrates.

SPECIFIC ACCOMPLISHMENTS:

Grant submitted:

NIH R21 "Animal Model for Inhalant Abuse" This grant application was submitted in collaboration with the Medical Department and received an excellent priority score of 192 by an NIH Review Committee.

Furthermore, this work is related to the studies supported by two currently funded NIH/NIDA projects: "PET Investigations of Abused Inhalants" and "Feto-maternal Pharmacokinetics of Abused Inhalants."

- College on Problems of Drug Dependence (CPDD) 65th Annual Meeting June 2003 Oral Presentation "*Toluene Inhalation Produces CPP in rats.*"
- *European Journal of Pharmacology (Submitted):* Gerasimov MR et al. "Toluene Inhalation Produces CPP in rats."

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$119,827 |
| FY 2003 | \$ 95,000 |

Project to Detect pp and ^7Be Solar Neutrinos in Real Time: LENS, the Low-Energy Neutrino Spectrometer

Richard L. Hahn

02-049

PURPOSE:

Neutrino detectors that have operated to date in real time at "low-energies" have observed either ^8B solar neutrinos at energies >5 MeV (SNO and Super-Kamiokande) or nuclear-reactor antineutrinos at energies >2 MeV (e.g., KamLAND). However, the only experiments that have detected solar neutrinos at energies <1 MeV (the energy range of the vast majority of solar neutrinos) have been the radiochemical detectors, the ^{37}Cl experiment at the Homestake Mine, and the ^{71}Ga experiments, GALLEX/GNO (in Italy) and SAGE (in Russia). The former experiment, with a threshold of 0.814 MeV, was sensitive to ^7Be and ^8B solar neutrinos; the latter, with a threshold of 0.233 MeV, is sensitive to the pp as well as the ^7Be and ^8B solar neutrinos. In 2002, SNO solved the thirty-year old Solar Neutrino Problem by obtaining definitive evidence that neutrinos oscillate from one neutrino flavor to another, and KamLAND then showed that antineutrinos also oscillate. There is current great interest in devising new experiments to detect the pp and ^7Be solar neutrinos in real time, to determine with high precision their fluxes and energy spectra, and their neutrino oscillation properties. This goal presents formidable challenges. LENS, the Low-Energy Neutrino Spectrometer project, is a promising approach to reaching this goal.

APPROACH:

Background levels in solar neutrino detectors, especially from naturally

occurring radioactivity such as the Th and U decay chains are formidable at very low energies. The approach in LENS is to detect neutrino capture in the detector/target (via a Charged Current neutrino interaction with a very low energy threshold) in a reaction that produces a specific coincidence "tag." In indium, the neutrino-capture reaction in ^{115}In has a threshold of 0.114 MeV and produces an electron, leading to an excited state in ^{115}Sn , which emits two gamma rays in rapid succession. This triple coincidence in time and in space serves as a definite signal for neutrino capture and strongly reduces non-correlated backgrounds in the detector.

The approach in LENS is to load the indium target into an organic liquid scintillator (an In-LS), to maximize the light production from neutrino interactions. The technical requirements are the preparation of an organic complex of indium that is (a) soluble in the organic LS (trimethyl benzene or mineral oil) at concentrations of $\sim 8\%$ by weight and (b) chemically stable (no formation of colloids, precipitates, or gels) over periods of years; and to have the LS have (c) high optical transparency and (d) high light output.

The LENS R&D effort in the Chemistry Department's Solar Neutrino Group has focused on developing chemical synthesis methods to produce the In-LS. Drs. Zheng Chang, Minfang Yeh, Alexander Garnov and the PI, R. S. Raghavan of Bell Laboratories-Lucent Technologies, and subcontractor C. Musikas did this work from Paris, France.

TECHNICAL PROGRESS AND RESULTS:

We focused mainly on the preparation of indium carboxylates in aqueous medium and their efficient transfer by solvent-solvent extraction into the organic LS. Our initial

work in 2002 used carboxylic acids that contained four or five carbon atoms, plus organic phosphorus compounds as the complexing agents. However, these were not so useful, in part because of their strong odors.

We focused in FY 2003 on the six-carbon methylvaleric acid (HMVA), without the organophosphorus compounds. We did systematic studies and prepared more than 100 different samples, varying parameters such as the concentration of indium, the ratio of concentrations of HMVA to indium, the concentration of ammonia needed to neutralize the HMVA to form methylvalerate ion (MVA), and the pH attained after the acidic aqueous indium-chloride solution was added to the system prior to the solvent extraction step. We used many analytical chemical methods to characterize the In-MVA in LS, such as colorimetric, titrimetric, and potentiometric measurements of the indium, MVA, and ammonia concentrations; the Karl Fisher method to determine water in the In-LS; x-ray fluorescence to determine chlorine in the In-LS; and IR spectroscopy to look for different In-organic species. We used UV-visible spectrophotometry to measure the light transmission in the In-LS; and built two systems, one with a 1-m pathlength of In-LS to measure the optical attenuation length, L (the distance light travels in the liquid until its intensity is reduced to $1/e$ of its initial value), and the other to determine the light output, S , of the In-LS excited by external gamma rays.

We monitored the time variation of L and S in studies of the long-term stability of the In-LS samples. We also began experiments to prepare solid samples of the In-MV to directly dissolve in the organic LS. This approach should be simpler and give purer product than the solvent-extraction method we have used.

Typical values attained in this work were attenuation lengths, $L \sim 2$ m, and light outputs, $S \sim 45\%$ (relative to the value from the neat organic scintillator liquid). These results are encouraging, but we will require larger values of L and/or S to achieve a multi-ton LENS neutrino detector with excellent background discrimination. Recent changes in our procedures have given encouraging results, and *we are keeping DOE and NSF informed of our progress.*

SPECIFIC ACCOMPLISHMENTS:

- 1) LENS – the Low-Energy Neutrino Project to Detect pp and 7Be Solar Neutrinos in Real Time Spectrometer, Hahn, R. L., at Conference on the Intersections of Particle and Nuclear Physics, New York, NY, May 19-24, 2003: (a) Talk presented on May 22; (b) Power Point presentation was posted on the Conference Web site; (c) Article for the Conference Proceedings is in press by the American Institute of Physics.
- 2) LENS – the Low-Energy Neutrino Spectrometer, Hahn, R. L., at NESS 02, Workshop on Neutrinos and Subterranean Science, Washington, D. C., September 19-21, 2002. The Power Point presentation was posted on the Workshop Web site.
- 3) LENS, Bowles, T. J. (LANL); Hahn, R. CIPANP 2003. L. (BNL); and Raghavan, R. S. (Bell Labs), submitted to National Research Council as input for the study “Neutrinos and Beyond: New Windows on Nature,” published by the Board on Physics and Astronomy of the NRC.
- 4) LENS R&D, and Testing of Prototype Detector Modules at LNGS, Hahn, R. L., at American Chemical Society Meeting, Symposium on Neutrino Oscillations, Boston, MA, August 17-18, 2002.
- 5) (Low-Energy) Solar Neutrinos, Hahn, R. L., at BNL Physics Department Workshop on Long Range Planning, October 14, 2003.

6) Results of LENS R&D at BNL, Hahn, R. L.; Chang, Z.; Yeh, M.; Garnov, A.; and Musikas, C., LENS Collaboration Semi-annual Meetings, Gran Sasso National Laboratory, Assergi, Italy, (a) September 22, 2003; (b) February 28, 2003; (c) September 20, 2002.

7) LENS, Kidd, M., student poster session at the meeting of the Division of Nuclear Physics, American Physical Society, Tucson, AZ, October 30, 2003.

One article, for the Proceedings of CIPANP 2003, is in press at the AIP; in two instances. One written document was presented to a Review Committee of the National Research Council.

LDRD FUNDING:

| | |
|---------|----------|
| FY 2002 | \$70,248 |
| FY 2003 | \$70,000 |

Combined Theoretical and Experimental Study of Crystal Lattice Defects in Complex Transition Metal Oxides

James W. Davenport

02-053

Y. Zhu

D. O. Welch

PURPOSE:

The purpose of this project is to provide first principles calculations of complex transition metal surfaces and compounds for comparison with experiments using the transmission electron microscope at BNL as well as x-ray studies from the National Synchrotron Light Source.

APPROACH:

First principles density functional calculations are being performed to obtain the energy, charge density and electron energy loss spectra for the relevant materials. These are obtained with the full potential linear augmented plane wave method and are run in parallel on the Linux cluster in the Center for Data Intensive Computing. Calculations of this type have not been compared previously in detail with experiments and there is a risk that the comparison will reveal that further advances in theory will be needed.

TECHNICAL PROGRESS AND RESULTS:

There was important progress in two systems which are examples of the joint theoretical and experimental program that is envisaged. First, because of the high spatial resolution of the transmission electron microscope it has been possible to study the angular dependence (relative to the

crystalline axes) of the electron energy loss spectra (EELS) in the newly discovered superconductor magnesium diboride. MgB_2 has not been available in large single crystals, so the TEM has been the only way to study angular effects since individual crystallites could be resolved. EELS spectra parallel and perpendicular to the crystalline c axis have been recorded and analyzed. First principles calculations have shown that the spectra can be understood in terms of the wave functions and matrix elements for the transitions from the core state to the unoccupied valence states. However, further work is needed to precisely define the angular behavior of the detectors and their energy resolution.

The second project is an outgrowth of the current interest in nanoscience. It has recently become possible to prepare linear chains of cobalt one atom wide and with lengths of approximately 80 atoms when adsorbed onto a stepped platinum surface. These chains have been investigated by magnetic circular dichroism and display the largest orbital magnetic moment (as opposed to spin moment) of any 3d transition element. Our first principles calculations model the system as a supercell with both cobalt and platinum. They show strong moments on the Co and essentially no moment on the Pt consistent with experiments. However, the magnitude of the orbital moment is lower by a factor of roughly 2 than the experimental one. This can be corrected with an empirical on site Coulomb interaction, but further work will be needed to fully understand the experimental results.

The final project involves the use of density functional theory to calculate the magnetic properties of the semiconducting compounds manganese arsenide, manganese antimonide, and manganese bismuth. These materials are promising candidates for so called

spintronics devices because they display the phenomenon of half metallic magnetism, meaning that there is an energy gap between the spin up and spin down states. We have computed the energy and stability of these materials in the zinc blende structure, and suggest that they could be grown epitaxially on gallium arsenide sunstrates.

SPECIFIC ACCOMPLISHMENTS:

Unraveling the Symmetry of Hole States near the Fermi Level in the MgB₂ Superconductor, Y. Zhu, A. R. Moodenbaugh, G. Schneider, J. W. Davenport, T. Vogt, Q. Li, G. Gu, D. A. Fischer, and J. Tafto. *Phys. Rev. Lett.* **88**, 247002 (2002).

Study of valence electron distribution in MgB₂ by accurate diffraction measurements and first principles calculations, L. Wu, Y. Zhu, T. Vogt, H. Su, J. W. Davenport, and J. Tafto, *Phys. Rev. B*, in press.

X-ray absorption study of the boron K near edge in MgB₂, A. R. Moodenbaugh, D. A. Fischer, Q. Li, G. Gu, Y. Zhu., H. Su, D. O. Welch, and J. W. Davenport, Submitted.

From the bulk to monatomic wires: An ab-initio study of magnetism in Co systems with various dimensionality, M. Komelj, C. Ederer, J. W. Davenport, and M. Fahnle, *Phys. Rev. B* **66**, 140407(R) (2002).

Comment on the analysis of angle-dependent X-ray magnetic circular dichroism in systems with reduced dimensionality, C. Ederer, M. Komelj, J. W. Davenport, and M. Fahnle, *J. Electron Spectroscopy and Related Phenomena*, **130**, 97 (2003).

Magnetic properties of MnAs in strained ZB and NiAs structure: predictions from all electron calculations, J.-C. Zheng and J. W. Davenport, *App. Phys. Letters*, Submitted.

Half-metallic ferromagnetism and stability of MnSb and MnBi in strained ZB structure: predictions from full potential and pseudopotential calculations, J.-C. Zheng and J. W. Davenport, *Phys Rev B*, Submitted.

LDRD FUNDING:

| | |
|---------|----------|
| FY 2002 | \$39,678 |
| FY 2003 | \$66,825 |

Chemical Sensors: Immobilization of Organo- metallic Complexes into Sol-gel Matrices

Mark W. Renner

02-055

PURPOSE:

Characterize the chemical and physical properties of porphyrin-based sensors encapsulated in sol-gel matrices for the detection of toxic chemicals and heavy metals. In order to develop porphyrin/sol-gel sensors, it is necessary to fully characterize and understand the effects the sol-gel matrix has on the spectroscopic properties of the sensor. This will aid in the rational design of sensors with enhanced selectivity and sensitivity.

APPROACH:

Previously, researchers have investigated the encapsulation of porphyrins into sol-gels or other polymers as sensors, magnetic materials, non-linear optic materials, and catalyst. Sol-gel matrices are attractive polymer supports due to their optical transparency and porous nature, as well as chemical, thermal, and structural stability.

This project will investigate the immobilization of porphyrin-based sensors into sol-gel matrices. The stability of the porphyrin-matrices and their reactivity will be monitored using a variety of spectroscopic techniques. Also, varying the porphyrins with different peripheral substituents, central metal ions, and axial ligands will be used in these studies. The methods to characterize these materials will consist of magnetic resonance techniques, optical and FT-IR spectroscopy. X-ray absorption techniques may be used to follow changes in the metals

oxidation, ligation and geometry upon sol-gel formation. Some of the porphyrins were provided through collaborations with K. Smith (Louisiana State University), M. Senge (Freie Universität Berlin), and D. Mansuy and P. Battioni (Université Paris V).

TECHNICAL PROGRESS AND RESULTS:

Synthetic methods were developed to prepare optically transparent porphyrin immobilized sol-gel monoliths. The siloxyl SiO^- groups of the sol-gel matrix were shown to form strong electrostatic interactions with metallo-porphyrins, cationic peripheral substituents and/or central metal ion. Coordination of the sol-gel siloxyl groups to the porphyrins central metal prohibits subsequent reactions, see Figure 1.

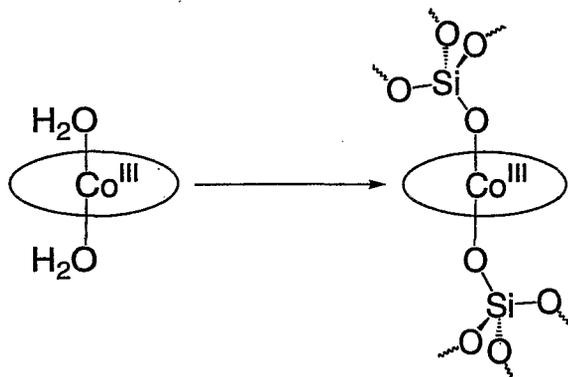


Figure 1. Reaction of Co(III)Porphyrin with the sol-gel siloxyl groups.

The metal can be protected during the sol-gel synthesis with axial ligands or surfactants. The resulting iron and cobalt porphyrin/sol-gels complexes show promising applications as chemical sensors for cyanide and amines.

Recently, it has been shown that porphyrins can be directly adsorbed onto the sol-gel surface to form films. These porphyrin films exhibit increased stability and reactivity compared to the porphyrins in solution and

encapsulated in sol-gels. Chemical reduction of the Co(III) porphyrins to Co(II) normally attacks and degrades the porphyrin in solutions; however, on the sol-gel surface the Co(II) porphyrin is stabilized from further reactions. Under aerobic condition the Co(II) is reversibly oxidized back to Co(III). The porphyrin films can be recycled for repeated uses and show detectable optical changes. The spectral changes upon binding one axial pyridine to a Co(II) porphyrin sol-gel film is shown in Figure 2.

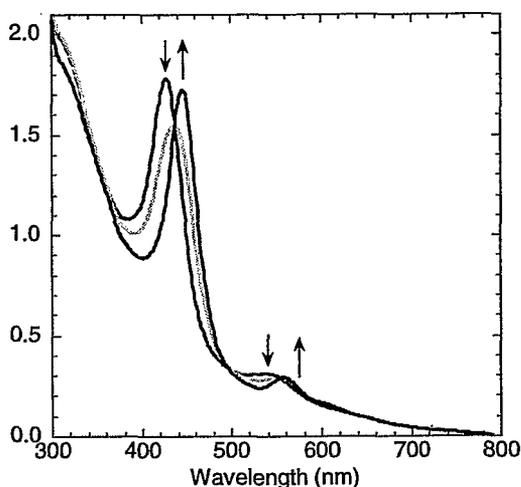


Figure 2. Optical change upon exposing Co(II) porphyrin sol-gel film (blue) in pH 7 phosphate buffer to pyridine (black) the arrow indicate the spectral evolution.

Another application of porphyrin films is the detection of cyanide, which is a chemical warfare agent and common industrial waste. Recently, copper porphyrins and myoglobin immobilized on glass surfaces have been used for the detection of cyanide. These sensors showed limited stability and have small optical absorption changes upon cyanide binding. The Co(III) porphyrin

films exhibit improved stability and optical changes, see Figure 3.

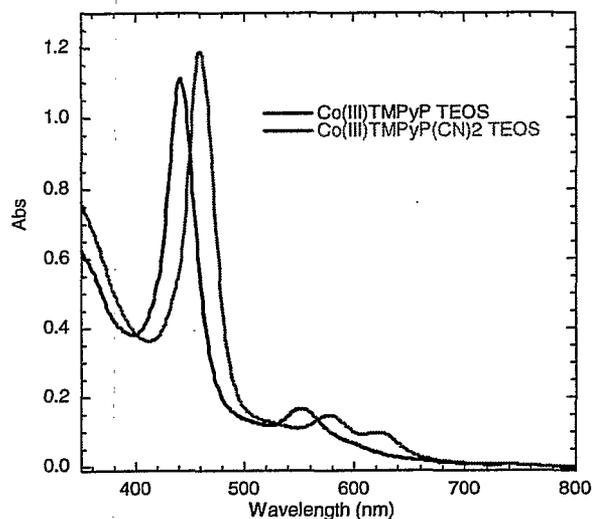


Figure 3. Optical spectra of Co(III)porphyrin solgel film before (blue) and after addition of cyanide (red), pH 7 phosphate buffer.

SPECIFIC ACCOMPLISHMENTS:

PET/Bio/Nano Mini Workshop at BNL March 2003. "Chemical Sensors: Immobilization of Porphyrins into Sol-Gel Matrices" M. W. Renner.

M. W. Renner "Metalloporphyrin Sol-gel Interactions: Applications as Chemical Sensors for Amines and Cyanide" manuscript in preparation.

LDRD FUNDING:

| | |
|---------|----------|
| FY 2002 | \$81,940 |
| FY 2003 | \$86,000 |

Size Dependence of Catalytic Reactivity of Iron Oxide Nanocrystals

Stanislaus S. Wong

02-056

PURPOSE:

The goal of the project is to synthesize and characterize iron oxide nanocrystals of a variety of different morphologies and sizes and to analyze the catalytic reactivity of these nanocrystals for the purpose of quinoline degradation; in addition to study the synthesis and characterization of ternary oxide perovskite nanotubes, which are also based on inorganic materials chemistry. This project has been a component of the BNL nanoscience initiative and of work related to the *Brookhaven Center for Functional Nanomaterials*.

APPROACH:

Nanocrystals are unique in that the number of surface atoms is a large fraction of the total and that their intrinsic properties are transformed by quantum size effects. Hence, they exhibit strongly size-dependent optical and electrical properties. Research on nanoparticles and nanotubes with size-dependent optical, chemical and electronic properties is motivated by potential applications, including those for novel optical components of catalytic converters with enhanced performance.

We have chosen to synthesize and then characterize novel iron-based nanostructures by carefully studying growth conditions in solution. Moreover, we have developed a hydrothermal synthesis technique for the production of inorganic-based perovskite nanostructures. With this data, we are currently then exploring the physical

dependence of the catalytic reactivity and optical properties of our nanomaterials.

TECHNICAL PROGRESS AND RESULTS:

I. Iron Oxide Nanoparticles.

We have characterized our iron oxide nanocrystals, synthesized in FY 2002, using UV-visible spectroscopy, electron microscopy, and infrared spectroscopy. We have indeed been able to form particles of varying aspect ratios (including spherical, peanut, ellipsoidal, spindle-type and platelet), based on using a number of different precursors and additives (i.e. varying concentrations of acid and base) as well as different reaction/aging times (ranging from minutes to weeks). Their sizes range from tens to hundreds of nm. In addition, we have begun to observe the reactivity of these nanocrystals (500 mg/L) in an aqueous solution of quinoline (10 mg/L) and 50% hydrogen peroxide (500 mg/L) for 1000 min of reaction time. We have observed preliminary differences in reactivity for instance, between using pseudocubic vs. platelet hematite nanocrystals, as an example.

II. Hydrothermal Synthesis of Crystalline BaTiO₃ and SrTiO₃ nanotubes.

One-dimensional nanotube/nanowire systems offer fundamental scientific opportunities for investigating the influence of size and dimensionality of materials with respect to their collective optical, magnetic, and electronic properties. As such, we have been intent on developing a mild, low temperature, and generalizable synthetic strategy to generate 1-D barium and strontium titanate perovskite nanotubes. To this end, we have developed a wet-chemical, hydrothermal synthesis, using an aqueous medium under alkaline conditions.

Hydrothermal synthesis of ceramic powders has been previously reported, especially for barium titanate. Typically, these reactions allow for the preparation of relatively phase-pure products under low temperatures and with control over reaction conditions such as concentration, pH, and temperature. Previous reports have focused on the reaction of a barium precursor such as Ba(OH)₂ and a titanium source such as titanium alkoxide, titanium tetrachloride, titanium oxide powder or a titanium oxide gel. Our strategy has been to utilize a titanium oxide (TiO₂) nanotube as a bona fide precursor material in order to generate the corresponding perovskite transition metal oxide nanotubes in a rational manner. It is expected that synthetic advances in achieving monodispersity and diameter control over the size distribution of TiO₂ nanotubes can certainly be extended to the predictive synthesis of perovskite nanotubes.

SPECIFIC ACCOMPLISHMENTS:

Yuanbing Mao, Sarbajit Banerjee, and Stanislaus S. Wong, "Hydrothermal Synthesis of Perovskite Nanotubes," *Chem. Commun.*, (3), 408-409 (2003).

Sarbajit Banerjee, Michael G. C. Kahn, and Stanislaus S. Wong, "Rational Chemical Strategies for Carbon Nanotube Functionalization," invited *Concepts* article, *Chem. Eur. J.*, **9(9)**, 1898-1908 (2003).

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Nanotubes by Solution-phase Ozonolysis," *J. Phys. Chem. B*, 106(47), 12144-12151 (2002).

"Rational Chemical Strategies for Carbon Nanotube Functionalization," invited presentation, IBM T. J. Watson Research Center, Yorktown Heights, NY, May 2, 2003.

"Nanoscale Strategies for Functionalization of Carbon Nanotubes," invited presentation, Chemistry Dept., Brookhaven National Lab, Upton, NY, February 26, 2003.

"Strategies of Carbon Nanotube Functionalization," American Vacuum Society 49th International Symposium, Denver, CO, November 4-8, 2002.

"Nanoscale Functionalization Strategies," invited presentation given in the Nanotechnology technical session at the 2nd Annual Emerging Information Technology Conference, Friend Center, Princeton University, Princeton, NJ, November 1-2, 2002.

Data from these studies were used as material in National Science Foundation (NSF) and American Chemical Society Petroleum Research Fund (ACS-PRF) proposals as well as in BNL nanoscience proposals, including "Understanding and Manipulating the Active Site in Catalytic Reactions," submitted to DOE in FY 2003.

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$ 84,575 |
| FY 2003 | \$104,000 |

Femtosecond Synchronization for Ultra-Short Pulse DUV- FEL Radiation

James Rose

02-058

W. Graves

J. B. Murphy

B. Sheehy

T. Shaftan

X. J. Wang

L. H. Yu

PURPOSE:

The objective of this work is to develop technologies to support Deep Ultra Violet Free-Electron Laser (DUV-FEL) research and development and future National Synchrotron Light Source (NSLS) upgrade. Synchronization between laser and electron beam plays an important role in both schemes for the possible future X-ray FEL (Free Electron Laser), such as self-amplified spontaneous emission (SASE) and the high-gain harmonic generation (HG HG). BNL is actively pursuing HG HG because of its many advantages over SASE, such as better radiation stability and longitudinal coherence. For HG HG to reach shorter wavelength, cascading of several stages of HG HG is necessary. Timing jitter control and electron beam qualities are two critical areas for the success of the cascaded HG HG. Timing control is critical for cascaded HG HG in three aspects. First, electron beam generation in a photo injector, where timing jitter between the photocathode RF gun drive laser and RF system needed is less than 500 fs. A factor of two improvements is required for the first stage laser seed in electron beam modulation. The fresh bunch technique in cascading multi-stage HG HG imposes even more stringent timing control, better than 100 fs.

APPROACH:

To develop technologies capable of delivering the performance required, we have a plan to attack these challenges on several fronts. First, we have identified that a laser and a low-level RF system are critical for timing control. Improvement of their environments, such as better temperature and vibration control, is the key. Second, we will develop femtosecond timing jitter diagnostics tools. Laser and RF (radio frequency) pickup will be non-interceptive techniques, which we are now investigating. Third, is feedback control of the timing jitter. Solid state S-band (2856 MHz) I-Q modulator will be developed for a low-level RF system.

TECHNICAL PROGRESS AND RESULTS:

During FY 2002, we have accomplished:

1. Solid State S-band I-Q modulator: Three sets of I-Q modulators (see picture below) were designed, constructed, and installed. We have demonstrated 0.1 degree (100 fs) RF control capability.
2. Electron beam and laser seed synchronization: We have demonstrated sub-picosecond synchronization between the electron beam and seed laser for HG HG and laser seeded FEL.
3. Success of HG HG and laser seeded FEL: The best illustration of the success of the timing control system is the saturation of laser seeded FEL and HG HG at 266 nm.

During FY 2003, we have accomplished: A new RF control system was designed and implemented to support short pulse High

Gain Harmonic Generation (HG) experiments, which require sub-picosecond synchronization between the laser and the accelerating RF fields. This control system consists of an 81MHz crystal oscillator to drive the Ti:Sapphire laser and uses the 81.6 MHz femtosecond pulse width laser pulses to generate the 35th harmonic at 2856 MHz. This harmonic is then filtered and amplified to drive the RF system. In addition, diagnostic techniques to resolve the femtosecond timing jitter were developed and are now a part of the DUV-FEL facility. The new system is shown schematically in Figure 1. Experimental results of synthesizing the RF directly from the 81.6 MHz pump laser pulse train compared to the old system is shown in Figures 2 and 3. Each plot consists of histograms of 8-second duration of a mixer-based phase error measurement. Figure 1 is for a laser oscillator and RF synthesizer driven from the same crystal. Figure 2 laser output pulses are filtered to drive RF directly. In each plot, the outside histograms are data taken by programming +/- 3 degree and +/- 2 degree steps, respectively, in the RF path for calibration.

DUV-FEL RF Synthesized From Laser Pulse Train

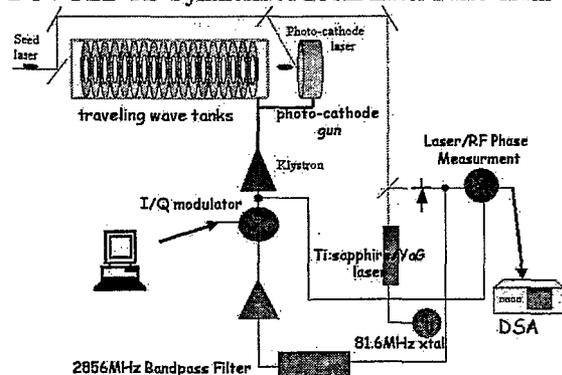


Figure 1. The new DUV-FEL low level RF system.

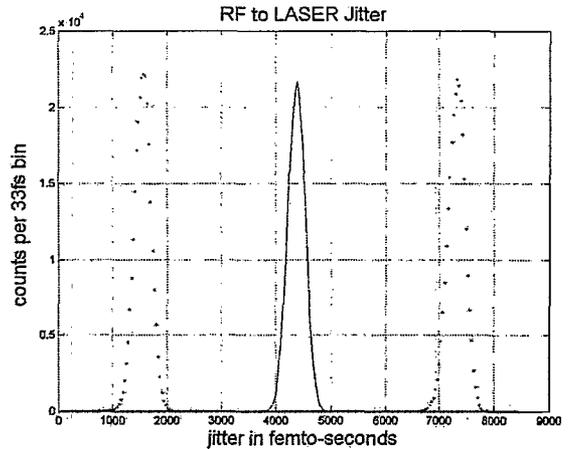


Figure 2. Jitter histogram with old RF system, 400 fs FWHM.

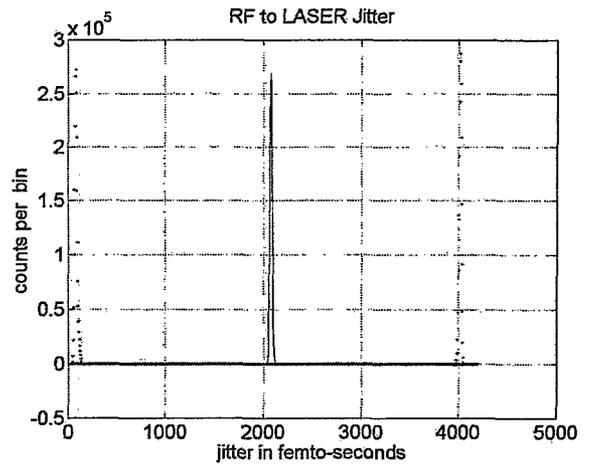


Figure 3. Jitter histogram with new RF system driven by laser oscillator output pulse train, showing <40 fs jitter FWHM.

The jitter between the RF and laser system (before the power amplifiers) has been reduced from ~400 fs FWHM to less than 40 fs FWHM, a factor of 10 improvement.

SPECIFIC ACCOMPLISHMENTS:

Publications:

W. Graves, "Microbunching and CSR Experiments at BNL's Source Development Lab," presented at the Workshop on Coherent Synchrotron Radiation and Its Impact on the Beam Dynamics of High-

brightness Electron Beams, DESY-Zeuthen, Berlin, Germany, January 14-18, 2002.

H. Loos, A. Doyuran, W. Graves, J. Rose, T. Shaftan, B. Sheehy, L. H. Yu, "Electron Bunch Compression and Coherent Effects at the SDL," Advanced Accelerator Concepts Workshop, Mandalay Beach, CA, June 23-28, 2002.

A. Doyuran, W. Graves, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, L. H. Yu, "Observation of SASE and Amplified Seed of the DUV-FEL at BNL," FEL 2002, Chicago.

A. Doyuran, W. Graves, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, L. H. Yu, "First SASE and Seeded FEL Lasing of the NSLS DUV-FEL at 266 & 400 nm," FEL 2002, Chicago.

L. H. Yu, L. DiMauro, A. Doyuran, W. S. Graves, E. D. Johnson, R. Heese, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, and Z. Wu, "First Ultraviolet High-Gain Harmonic-Generation Free-Electron Laser," Physical Review Letters, Vol 91, No. 7.

A. Doyuran, W. Graves, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, L. H. Yu, "Observation of SASE and Amplified Seed of the DUV-FEL at BNL," NIM Methods in Physics Research A 507 (2003) 392-395.

L. DiMauro, A. Doyuran, W. Graves, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, L. H. Yu, "First SASE and Seeded FEL Lasing of the NSLS DUV-FEL at 266 and 400nm," NIM Methods in Physics Research A 507 (2003) 15-18.

J. Rose, A. Doyuran, W. Graves, H. Loos, T. Shaftan, B. Sheehy, Z. Wu, "Radio Frequency Control System for the DUVFEL," Proceedings of the 2003 Particle Accelerator Conference, Portland.

Awards

2003 Free Electron Laser Prize, Li Hua Yu, "In recognition of his outstanding contributions to FEL science and technology."

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$134,883 |
| FY 2003 | \$135,000 |

Rapid Wavelength Tunability for the DUV-FEL

Brian Sheehy

02-062

PURPOSE:

The deep ultraviolet free electron laser (DUVFEL), a combination user facility and development project of the NSLS, is proving itself both a valuable new scientific tool and an important test bed for the development of new sources. It has had and will have important impacts on the design of next-generation sources, and its applied experimental program is opening new territory in chemical dynamics. The purpose of this LDRD is to develop techniques necessary to assure the flexibility needed to smoothly and rapidly tune and configure the machine for both the user and source development programs.

This work was carried out by the scientists and postdocs collaborating in the DUVFEL: G. L. Carr, Louis DiMauro, Adnan Doyuran, William Graves, Richard Heese, Steve Hulbert, Erik Johnson, Henrik Loos, Jim Murphy, Jim Rose, Sam Krinsky, George Rakowsky, Timur Shaftan, John Skaritka, Xijie Wang, Zilu Wu, and Li Hua Yu.

APPROACH:

The facility includes an ultrafast laser system that generates the electron bunch in the RF gun, provides seed radiation to generate coherent FEL output, and produces reference beams for various diagnostics and experiments. Smooth control requires integrating these functions with control of the electron beam dynamics in a seamless way. Accomplishing this requires significant development on several fronts: seed light generation, transport and

synchronization, beam and output diagnostics, and beam machine controls.

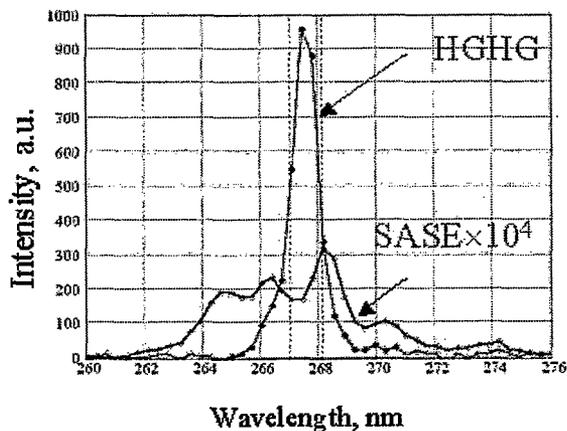
Generation of a stable seed requires temporal shape control independent of the photocathode drive pulse that generates the electron bunch. This is done with a separate compression stage for the amplified infrared pulse, with the proper seed wavelength synthesized using nonlinear optical methods. As pulse temporal profiles are critical in both seed and drive pulse, high-resolution diagnostics had to be developed, and methods of pulse-shaping are highly desirable. Pulse shapes are measured by cross-correlation with the oscillator. Optimally, pulse shaping would be done coherently, modulating spectral amplitude and phase in the oscillator pulse. As this requires some investment, we have used simpler methods first to do some important proof-of-principle experiments.

Transport and synchronization of the seed require an optical relay stable over the 35 meter transport distance and diagnostics to control synchronization and spatial overlap with the electron beam. At the same time, electron beam parameters must be rapidly measured and optimized. All of this is integrated into the control system for the machine as a whole, in order that both optical and electron beam parameters can be cooperatively controlled. Output diagnostics are required to analyze the spectral, temporal, and spatial characteristics of the output beam.

TECHNICAL PROGRESS AND RESULTS:

We have completed the construction of an independent pulse compressor and frequency tripler for the direct seeding of the FEL. A stable transport line was designed and constructed, first for 266 nanometer light, intended to directly seed the FEL, and

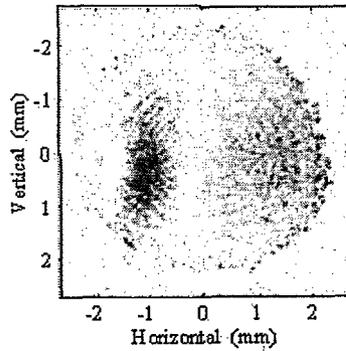
subsequently for 800 nm light, which is used in High Gain Harmonic Generation (HG HG). HG HG is a technique in which the FEL is seeded by a subharmonic of the desired output radiation in a separate undulator. The resultant energy modulation induces microbunching in the electron bunch in a following dispersive section, and this yields coherent radiation at the shorter wavelength in the radiator. Spectral profiles are shown below, showing the dramatic line-narrowing indicative of HG HG relative to the much weaker ($\sim 10^{-4}$) self-amplified spontaneous emission (SASE) that is emitted in the absence of the seed. The HG HG has been driven to saturation, tunability through variable synchronization with the seed has been demonstrated, and experiments exploring the feasibility of chirped-pulse amplification have been done.



An output diagnostic end station has been implemented for spectral, temporal, and spatial analysis of the FEL output. An extensive electron-beam monitoring system comprising Ce:YAG pop-in monitors was integrated with an optical alignment system and computer control to permit rapid beam alignment and electron bunch measurements including emittance, slice emittance, and high-resolution temporal profiles. This has reduced the beam alignment and matching time to minutes. Pop-ins also permit step-

wise measurement of the output build-up in the radiator. Scanning and single-shot cross-correlators and autocorrelators have been designed and constructed for temporal characterization of drive, seed, and output beams. Using the above diagnostics, we have refined new techniques of time-resolved measurement of beam parameters and conducted extensive studies on beam dynamics during compression, an issue critical to FEL development. We have also shaped the temporal profile of the photocathode drive pulse, and studied its effects on beam dynamics and radiation from the electron bunch. This has proven to be a very useful tool in studying electron bunch dynamics questions that are critical to future FEL development, and for pursuing the promising question of using modulated electron bunches to generate intense Terahertz radiation.

We have developed electro-optical detection methods both for measuring the electron bunch profile and for measuring both the spatial and temporal *electric field* profile of Terahertz radiation generated by transition radiation. The figure below shows a two-dimensional representation related to the transverse field distribution in a 130 fsec time slice near a focus of the terahertz pulse (the characteristic radial polarization of transition radiation may be seen in the sign change through the origin). This exciting new Terahertz source is almost two orders of magnitude more intense than laser sources, and opens a new realm of possibilities in Terahertz spectroscopy.



SPECIFIC ACCOMPLISHMENTS:

L.H. Yu et al. *First Ultraviolet High-Gain Harmonic Generation Free Electron Laser*. Physical Review Letters 91, 074801 (2003)

A. Doyuran et al. *Experimental Study of a High-Gain Harmonic-Generation Free-Electron Laser in the Ultraviolet*. submitted to Physical Review Special Topics, Accelerators and Beams

L. Dimauro et al. *First SASE and seeded FEL lasein of the NSLS DUV FEL at 266 and 400 nm*. Nucl Inst & Meth. A 507, 15 (2003)

A. Doyuran et al. *Observation of SASE and amplified seed of the DUV-FEL at BNL* Nucl Inst & Meth. A 507, 392 (2003)

J.G. Neumann et al. *Electron beam modulation using a laser-driven photocathode*. Nucl Inst & Meth. A 507, 498 (2003)

H. Loos et al. *Electron Bunch Compression and Coherent Effects at the SDL*. in Advanced Accelerator Concepts: Tenth Workshop. AIP Conference Proceedings no. 647, p .849 (2002)

A. Doyuran et al. *Diagnostics System for the NISUS Wiggler and FEL Observations at the BNL Source Development Laboratory*. European Particle Accelerator Conference Paris, France, June 3-7, 2002 (hereafter "EPAC'02" papers available online through JACoW)

H. Loos, et al. *Experiments in Coherent Radiation at SDL*. EPAC'02

T. V. Shaftan et al. *Electron Bunch Compression in the SDL Linac*. EPAC'02

T. V. Shaftan et al. *Beam-based Trajectory Alignment in the NISUS Wiggler*. EPAC'02

H. Loos et al. *Electro-Optic Longitudinal Electron Beam Diagnostic at SDL*. 2003 Particle Accelerator Conference, 12-16 May 2003, Portland Oregon (hereafter "PAC'03", papers available online at http://warrior.lbl.gov:7778/PAC_PUBLIC/search.html)

T. Shaftan et al. *Microbunching and Beam Break-up in DUV-FEL*. PAC'03

J. Rose et. al. *Frequency Control System for the DUVFEL*. PAC'03

G. L. Carr et al *Coherent THz Pulses from Relativistic Electrons*. Frontiers in Optics/Laser Science XIX, 87th Annual Meeting of the OSA, 5-9 October 2003, Tucson, Arizona. (ThT3).

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$135,269 |
| FY 2003 | \$135,000 |
| FY 2004 (budgeted) | \$135,000 |

High-Gain Harmonic-Generation at the DUV-FEL

Li Hua Yu

02-066

PURPOSE:

Investigate the performance of a high-gain harmonic-generation (HG HG) free-electron laser at the Deep Ultra Violet-Free Electron (DUV-FEL) facility. The HG HG approach utilizes a laser-seeded FEL to produce amplified, longitudinally coherent, Fourier-transform-limited output at a harmonic of the seed laser. Previously, we successfully demonstrated the HG HG FEL in the infrared in an experiment performed at the BNL/Accelerator Test Facility (ATF). Recently, we have carried out the Self Amplified Spontaneous Emission (SASE) experiment at 400 nm using Near Infra-red Scalable Undulator System (NISUS). Here, we plan to extend this work into the visible and then down to 100 nm at the DUV-FEL. In the long-term development of the HG HG 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. To accomplish this, it will be necessary to cascade several stages of high-gain harmonic-generation. Therefore, in addition to the experimental investigations at the DUV-FEL facility outlined above, we plan to carry out theoretical studies of the cascading process, investigating its potential and sensitivities.

APPROACH:

The conventional approach to X-ray FEL is to use the SASE method. The SASE output is not longitudinal coherent as its bandwidth is larger than spontaneous radiation. Our theory showed that using HG HG approach, we can achieve coherent output with stable,

narrow bandwidth output. We use the photo-cathode RF electron gun and the NISUS undulator at the Source Development Lab (SDL) to demonstrate the HG HG operation and generate DUV output for application in chemistry. The collaborators include A. Doyuran, H. Loos, T. Shaftan, B. Sheehy, W. Graves, and J. Murphy.

TECHNICAL PROGRESS AND RESULTS:

During FY2002, we accomplished SASE at 400 nm, at 266 nm and achieved near saturation of seeding at 266 nm. These showed that the trajectory in the NISUS undulator and the electron beam quality is appropriate for HG HG to generate 266 nm radiation from 800 nm with a micro joule output at 88 nm. Based on this result, we installed the modulator and dispersion magnet.

In FY 2003, we installed seeding optics for 800 nm input, and commissioned the new electron beam line. In short, we have achieved three milestones: 400 nm SASE, 266 nm SASE and 266 nm seeding. After the commissioning of the new electron beam line with the modulator, dispersion magnet and the seeding beam line in October we succeeded in achieving saturated HG HG output at 266 nm. We accomplished the characterization of the HG HG output. The results showed that we had obtained nearly complete coherence with one-tenth less bandwidth than SASE, saturation at 5 meter into the NISUS wiggler, in excellent agreement with theory. The work has generated positive responses from many different labs around the world. The theoretical work in parallel with this experiment has shown the possibility of cascading HG HG in only two stages to achieve soft X-ray FEL. The experiment also pointed out a promising scheme to

realize unprecedented accurate synchronization between the seed laser and the electron bunches.

SPECIFIC ACCOMPLISHMENTS:

Acquired funding from the Air Force Office of Scientific Research/Finance Department (AFOSR/PIF), Medical FEL Research Program, Agreement Number NMIPR015203751.

Publications:

- L. H. Yu, A. Doyuran, L. DiMauro, W. S. Graves, E. D. Johnson, R. Heese, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, Z. Wu, "First Ultraviolet High-Gain Harmonic-Generation Free Electron Laser," PRL, 91, 7, 074801 (2003)
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- T. V. Shaftan, A. Doyuran, H. Loos, L. H. Yu, S. Mikhailov, J. Skaritka, S. Krinsky, W. Graves, B. Sheehy, E. D. Johnson, J. Wu, J. Rose, Z. Yu, J. Rakowsky, "Beam-based trajectory alignment in the NISUS undulator," EPAC 2002.
- T. V. Shaftan, A. Doyuran, W. Graves, E. D. Johnson, S. Krinsky, H. Loos, J. Rose,

J. Skaritka, B. Sheehy, J. Wu, L. H. Yu, Z. Yu, "Electron bunch compression in SDL linac," EPAC 2002

- A. Doyuran, W. Graves, E. D. Johnson, S. Krinsky, H. Loos, G. Rakowsky, J. Rose, T. V. Shaftan, B. Sheehy, J. Skaritka, J. Wu, L. H. Yu, "Diagnostic System of the NISUS Wiggler and FEL Measurements in SDL," EPAC (2002)Presentations:

- Li Hua Yu, Juhao Wu, "Theory of High Gain Harmonic Generation-an Analytical Estimate," Proceedings of 23'th International Free Electron Laser Conference, Darmstadt, August 20-24, 2001
- A. Doyuran, W. Graves, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, J. Skaritka, X. J. Wang, L. H. Yu, "Observation of SASE and Amplified Seed of the DUV-FEL at BNL," FEL 2002, Chicago
- A. Doyuran, W. Graves, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan*, B. Sheehy, J. Skaritka, X. J. Wang, L. H. Yu, "First SASE and Seeded FEL Lasing of the NSLS DUV FEL at 266 & 400 nm," FEL 2002, Chicago
- A. Doyuran, L. DiMauro, R. Heese, E. D. Johnson, S. Krinsky, H. Loos, J. B. Murphy, G. Rakowsky, J. Rose, T. Shaftan, B. Sheehy, Y. Shen, J. Skaritka, X. J. Wang, Z. Wu, L. H. Yu, "Preliminary Chirped Pulse Amplification of HGHG-FEL at DUV-FEL Facility in BNL," Proceedings of FEL 2003, Tuskuba, Japan (2003)

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$134,947 |
| FY 2003 | \$135,000 |

Biom mineralization: a Route to Advanced Materials

Elaine DiMasi

02-067

PURPOSE:

Advances in nanotechnology will require the ability to control the structure, morphology and hierarchical organization of composite materials and macromolecular assemblies: precisely the qualities evident in biological materials and systems. Pursuit of biomimetic materials proceeds on a number of fronts, including the study of solution growth methods (i.e. inorganic physical chemistry), macromolecular self-assembly (organic and bio-chemistry) and the use of biological tools such as gene design and expression of designer proteins fixed on substrates where they interact in assemblies. Our program has focused on biomimetic mineral systems, with synchrotron x-ray methods that provide unique information about the structure and in-situ growth characteristics. This research is one cornerstone of BNL Physics and NSLS Department initiatives in the nanoscale physics of soft condensed matter systems and has formed part of the science cases for instrumentation proposals such as new synchrotron microbeam capabilities and the future NSLS-II light source.

APPROACH:

Biological mineralization occurs in an aqueous environment, which provides the mineral salts along with additional metals and macromolecules, which strongly affect the kinetics of mineralization and are able to select the mineral crystal type and morphology. In many instances further control is exerted by the presence of an insoluble matrix or template. One central question in the field regards the mechanisms

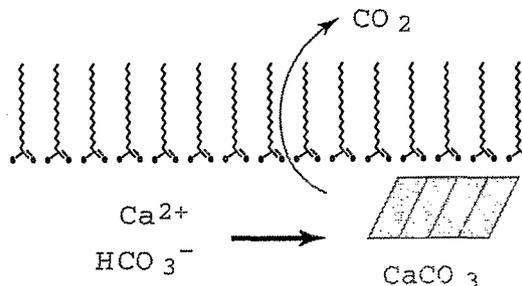
by which the template affects mineralization. Our innovation is to use surface-sensitive x-ray scattering methods, which are sensitive to the structures of the pre-existing matrix along with the nucleating mineral. Work was performed on CaCO_3 mineralization at Langmuir films and on solid film substrates.

Two additional aspects of our program include microstructure studies of biological minerals such as abalone shell, carried out at NSLS microbeam lines and electrochemical studies of titanium alloy implant materials designed for enhanced compatibility with living bone.

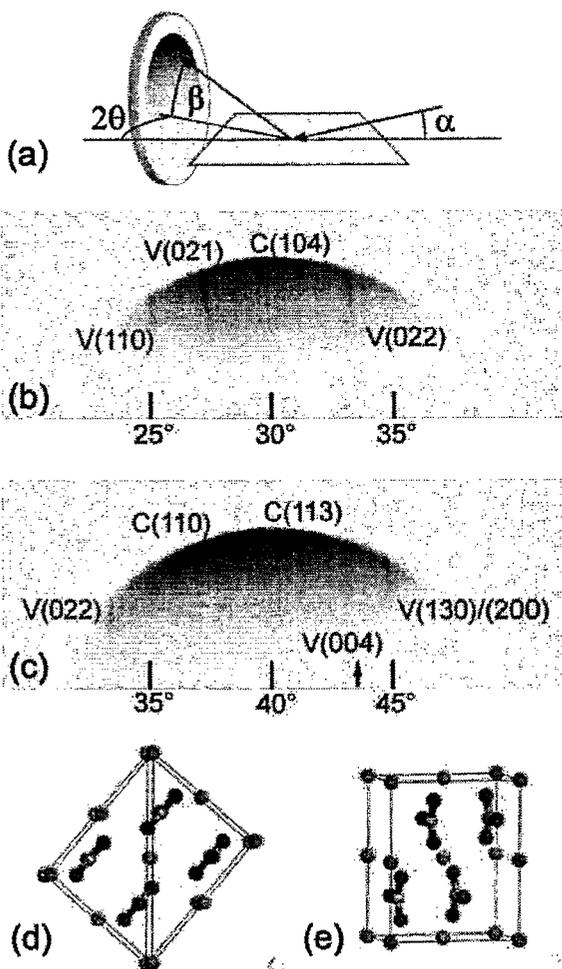
Collaborators include Laurie Gower (U. Florida, Gainesville) who studies polymer-induced amorphous mineral precursors; Christine Orme (LLNL) in electrochemistry of coated titanium bone implant alloys; Mehmet Sarikaya (U. Washington, Seattle) provided marine biom mineral samples; Nadine Pernodet and Miriam Rafailovich (SUNY-SB) assisted with atomic force microscopy (AFM), polymer and protein coating experiments. Tianbo Liu (BNL Physics) collaborated on laser light scattering experiments on polymer-induced mineralization.

TECHNICAL PROGRESS AND RESULTS:

In Fiscal Year 2002, we completed an assessment of the mechanisms controlling CaCO_3 mineralization at organic monolayers on water depicted schematically below.



In these systems there is a pervasive belief that crystals are structurally templated by the films as they nucleate. Our surface x-ray scattering studies demonstrated conclusively that this is not the case for calcium carbonates at liquid surfaces. Instead, both the insoluble organic film and the soluble macromolecules act by kinetic effects: the balance of gas diffusion against charge gradients completely dictates the outcome of mineralization. Our x-ray work has been very well received in the field and recognized as unique.



NLSL instrumentation developed to achieve these results included the integration of an area detector (above a) capable of acquiring mineral diffraction patterns (b and c) at

liquid surfaces, to detect crystal alignment (d and e).

In Fiscal Year 2003, we completed a detailed assessment of the effects of cation binding, metal additives, and polymer concentration. Some of this work, which involved extensive systematic exploration of solution parameters, is still in the process of being analyzed and reported. We also extended our studies to include lipid films, which are the components of membranes and are thus biologically much more pertinent than the fatty acid layers. No conclusive general results from lipid films have been achieved, but the indications so far are that a significant headgroup charge is necessary for a template to affect mineralization.

This being the case, we concentrated most recently on mineralization at solid supports and surfaces, where localized charges can be pinned. The first project of note involves Ti alloys which are used as bone implant materials. These materials acquire a “dome” morphology in their native oxide when in the presence of electrochemically corrosive environments, such as wounds. Within-situ x-ray observations of titanium/alloy surfaces etched with hydrogen peroxide, we began to characterize the surface reactions. The next step for this work is to correlate the surface reactivity with the electrochemical growth of calcium phosphate (i.e. bone mineral) on the metal for eventual medical application.

Another direction now underway is the development of eggshell-mimicking substrates for CaCO_3 growth. Silicon surfaces coated with a variety of functionalized organics, ranging from silane films to spin-coated polymers to keratin sulfate proteins, are under study and will be subjected to mineralization in solution under conditions known to produce oriented macroscopic crystals. In these systems, the

early growth times have still not been probed and we expect significant new results.

SPECIFIC ACCOMPLISHMENTS:

Programmatic Funding

A Proposal for an X-ray Micro-diffraction Instrument at the NSLS X13B Mini-Gap Undulator Beamline, DOE LAB03-03, NSLS, funded \$815K FY 03-04.

Nanotemplate Directed Assembly of Soft and Biomaterials, NSET, BNL Physics/NSLS, funded FY 03-05. Funds provide lab space and an AFM facility in partial support of biomineralization research.

Engineering Titanium for Improved Biological Response, LLNL, LDRD funded FY 03. Supports bone implant coating work.

Publications:

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When is Template Directed Mineralization Truly Template Directed? E. DiMasi et al, CrystEngComm **5** (2003) 346.

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Amorphous CaCO₃ Film Formation at Langmuir Films: I. Cation Binding and

Headgroup Charge; and II. Effects of Polymer Inhibitors. E. DiMasi, L. B. Gower, et al, in preparation.

Laser Light Scattering Studies of a Polymer-Induced Liquid Precursor Process for Mineralization. E. DiMasi, T. Liu, M. J. Olszta and L. B. Gower, in preparation.

Internal Reports:

Effect of Hydrogen Peroxide on the Native Oxide of a Titanium Surface. E. DiMasi, C. Orme, J. Bearinger, J. Muyko.

Growth Rate of Polymer-induced Calcium Carbonate Films: Concentration and CO₂ Dependence. E. DiMasi, V. M. Patel, M. J. Olszta, M. Sivakumar, G. Sivakumar, Y. P. Yang, L. B. Gower.

Microdiffraction from Abalone Shell: Microstructure and Crystallite Orientation at the Nacre-prismatic Boundary. E. DiMasi and M. Sarikaya.

Presentations and Reviews:

DOE-BES review, December 2001

LDRD review, April 2002, 2003

5 seminars: BNL, SUNYSB, UC Boulder

Direct Observation of Mineralization at a Monolayer Template by Synchrotron X-ray Scattering. DiMasi, E.; Patel, V. M.; Olszta, M. J.; Sivakumar, M.; Sivakumar, G. R.; Yang, Y. P.; Gower, L. B. contributed poster at Materials Research Society Fall Meeting, Boston MA, 2-4 Dec. 2001.

Direct Observation of Mineralization at a Monolayer Template by Synchrotron X-ray Scattering. DiMasi, E.; invited talk at United Engineering Foundation Conference on Biomimetic Engineering, Destin FL, 3-6 March 2002.

Direct Observation of Biomimetic Mineralization by Synchrotron X-ray Scattering. DiMasi, E.; Patel, V. M.; Olszta, M. J.; Sivakumar, M.; Sivakumar, G. R.; Yang, Y. P.; Gower, L. B.; contributed talk at Materials Research Society Spring Meeting, San Francisco CA, 2-5 April 2002.

In-situ Studies of Biomimetic Thin Films. DiMasi, E., invited talk at Frontiers for Synchrotron Research on Soft Matter and Biomaterials Workshop, sponsored by BNL, Tarrytown NY 25-27 April 2002.

When is Template Directed Mineralization Really Template Directed? DiMasi, E.; Patel, V. M.; Olszta, M. J.; Sivakumar, M.; Sivakumar, G. R.; Yang, Y. P.; Gower, L. B.; contributed poster at Gordon Research Conference on Biomineralization, New London NH 11-16 August 2002.

When is Template Directed Mineralization Really Template Directed? DiMasi, E., invited talk at Materials Research Society Spring Meeting, San Francisco CA, April 2003.

Biophysics Applications of Liquid Surface Scattering. E. DiMasi, poster for Biophysics Workshop at NSLS Users' Meeting, BNL, May 2003.

Laser Light Scattering Studies of a Polymer-Induced Liquid Precursor Process for Mineralization. E. DiMasi, T. Liu, M. J. Olszta, and L. B. Gower, contributed poster at Materials Research Society Meeting, Boston MA, 2 Dec 03.

Synchrotron X-ray Microbeam Diffraction from Abalone Shell. E. DiMasi and M. Sarikaya, to be submitted as contributed posters at 2003 APS March Meeting (Montreal Canada) and Gordon Research Conference on Biomineralization.

Recognition by Materials Research Society, December 2001.

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$ 99,935 |
| FY 2003 | \$105,400 |

Theory of Electronic Transport in Nanostructures and Low-Dimensional Systems

Alexei M. Tsvelik

02-070

PURPOSE:

To study combined effects of strong correlations, low dimensionality, and disorder on transport properties and correlation functions. All three factors determine the physics of nanoscale systems, and hence their understanding is crucial to creation of nanoscale technology.

APPROACH:

Correlation effects are especially strong in low-dimensional systems due to strong quantum and thermal fluctuations. For this reason perturbation theory does not work, and one needs to use more sophisticated methods. In our studies we use the methods developed in the theory of integrable systems combining them with such non-perturbative techniques as bosonization and conformal field theory.

We are interested in fundamental problems of physics of strongly correlated systems, such as existence of fractional quantum number excitations in dimensions higher than one and in detailed studies of realistic one- and zero-dimensional (quantum dots) systems. The latter ones are important for nanotechnology.

The collaborators include M. J. Bhaseen and R. Konik (both are postdoctoral associates) and F. H. L. Essler.

TECHNICAL PROGRESS AND RESULTS:

In FY 2002, we found a model of a three-dimensional frustrated antiferromagnet which displayed fractional quantum number excitations (spinons). The approach was based on exact solution. The work done in FY 2003 with Bhaseen is a development of these ideas. Here we compared the exact results with the popular $1/N$ -approximation and found that the latter was not a reliable tool. We also completed a work on description of neutron spectra of realistic Mott insulators. In addition, new work on Fano resonances was done by R. Konik. It is related to the microstructure of conductivity in quantum dots.

SPECIFIC ACCOMPLISHMENTS:

Publications:

Bhaseen, M. J.; Tsvelik, A. M. SU(N) Evolution of a Frustrated Spin Ladder. *Phys. Rev. B* **68**, 094405 (2003).

Bhaseen, M. J.; Essler, F. H. L.; Grage, A.: Itineracy Effects on Spin Correlations in 1D Mott Insulators, to be submitted to Physical Review Letters.

Eichmann, U.; Gallagher, T.; and Konik, R: Reply to Comment on "Fano Line Shapes Reconsidered: Photoionization Peaks from Pure Continuum Excitation (PRL 90, 233004 (2003))," submitted to Physical Review Letters.

Eichmann, U.; Gallagher, T.; and Konik R.: "Theory of Fano Resonances in the Photo-emission Spectrum of Sr^{++} ," to be submitted to Physical Review A.

Konik, R.: "Fano Resonances in Quantum Dots: The Non-perturbative Role of Potential Scattering," to be submitted to Physical Review B.

Konik, R.: "Exact Transport Properties of Multiple Quantum Dots," to be submitted to Physical Review B.

Konik, R.: "Non-perturbative Studies of Dimerized Integer Spin Chains," to be submitted to Physical Review B.

Conferences:

Bhaseen, M. J. Conference Coordinator for "International Workshop on Field Theory

Methods in Correlated Nanoscale Systems," August 26 -30, 2003, held at BNL.

Konik, R. M., "Non-perturbative Topology of Fano Resonances in Quantum Dot," Workshop on Field Theory Methods in Correlated Nanoscale Systems, Brookhaven National Laboratory, Upton, NY, August 26-30.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$134,268 |
| FY 2003 | \$115,000 |
| FY 2004 (budgeted) | \$145,500 |

Pressure in Nanopores

Thomas Vogt

02-071

Y. Lee

PURPOSE:

The purpose of this project is to study the structural changes occurring in nanosystems, which results from pressure-induced chemical reactions or intercalations within nanopores, channels and layers. Various interactions between the species, inherent in a given nanosystem or introduced under pressure, lead to unusual property changes via pressure-induced volume expansion, formation of ordered water nanotubes or chains, or trap-door ion-exchange, which may open new types of applications of these materials.

APPROACH:

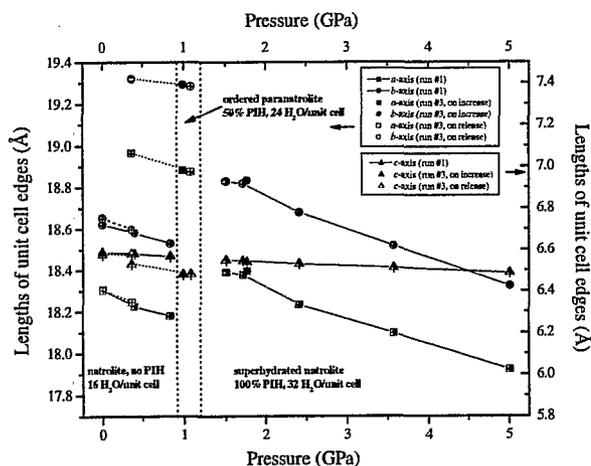
We used micro-focused monochromatic synchrotron X-ray powder diffraction and diamond-anvil high-pressure cells at beamline X7A of National Synchrotron Light Source (NSLS). Structural studies are carried out using either the Rietveld technique or *ab initio* structure solutions. We propose the use of a hydrothermal DAC and He refrigerator to extend our thermodynamic space into unexplored P-T regions. In addition, pressure effects on nanolayer systems and nanoparticles are currently being investigated.

Main collaborators are J. A. Hriljac (U Birmingham, UK), C. C. Homes (Physics, BNL), J. B. Parise (USB), J. E. Post (Smithsonian), S.-W. Chan (Columbia Univ.), H. ZurLoye (USC), A. Ulman (Polytech Univ.), Brendan Kennedy (University of Sydney).

TECHNICAL PROGRESS AND RESULTS:

In FY 03, we have continued investigating pressure effects on nanopore-materials using the high pressure experimental technique

described above. Among those we have for the first time, experimentally observed the controversial parnatrolite phase and solved its unknown structure, the largest yet known volume expansion (~7%) via partial pressure induced hydration. We demonstrate here that specific water-cation coordination network dictates the geometry of the host nanochannel (or vice versa) and propose that this phase may be an ideal host for trap-door ion exchange in radioactive ion (Sr, Cs...) clean up or as a drug delivery vehicle (Gd).



Pressure-evolution of natrolite at room temperature showing the ordered parnatrolite phase via partial pressure-induced hydration

In addition, we are currently implementing high-pressure IR measurements at beamline U10A (in collaboration with C. Homes of Physics) and high-pressure magnetic property measurement using MPMS (in collaboration with C. Petrovic of Physics).

SPECIFIC ACCOMPLISHMENTS:

Awards

1. MSA Crystallographic Research Grant Award (2004), Mineralogical Society of America.

Invited talks

1. In situ High-pressure Synchrotron X-ray Powder Diffraction Study of Tunnel Manganese Oxide Minerals. In *the Charles*

Prewitt Session, the 2003 MSA Annual Meeting at the Geological Society of America Annual Meeting, Seattle, WA. (talk given by J.E. Post).

2. High-Pressure Powder Diffraction on Zeolites at NSLS. In *the Mineral Physics Institute Seminar*, SUNY Stony Brook, Feb. 5, 2003.

3. High-Pressure Powder Diffraction on Zeolites at NSLS. In *the Friday Seminar*, National Synchrotron Light Source, Jan. 24, 2003

Publications

1. Lee, Y.; Hriljac, J. A.; Parise, J. B.; Vogt, T.; Pressure-Induced Stabilization of Ordered Parantrolite: A Solution to the Parantrolite Controversy and Its Application to Trap-Door Ion-Exchange (submitted) *Nature*.

2. Jeong, I. -K.; Darling, T. W.; Graf, M. J.; Proffen, T.; Heffner, R. H.; Lee, Y.; Vogt, T.; and Jorgensen, J. D.; (submitted) The Role of the Lattice in the Ce gamma-alpha Phase Transition: a High Pressure Neutron and X-ray Diffraction Study. *Phys. Rev. Lett.*

3. Kennedy, B. J.; Li, L.; Lee, Y.; and Vogt, T.; (submitted) Pressure Induced Valence and Structural Phase Transition in Ba₂PrRu_{1-x}Ir_xO₆. *Phys. Rev. B*

4. Park, S.; Lee, Y.; Moodenbaugh, A.; and Vogt, T.; (in press) Novel Synthesis and High Pressure Behavior of Na_{0.3}CoO₂x1.3H₂O and Related Phases. *Phys. Rev. B*.

5. Lee, Y.; Petrovic, C.; Vogt, T.; and Canfield, P. C.; (submitted) Structural Response of the Spin State Transition in FeSb₂. *Phys. Rev. B*.

6. Lai, J.; Shafi, K. V. P. M.; Loos, K.; Ulman, A.; Lee, Y.; Vogt, T.; and Estrones, C.; (2003) Doping g-Fe₂O₃ Nanoparticles with Mn(III) Suppresses the Transition to the a-Fe₂O₃ Structure. *J. Am. Chem. Soc.* 125: 11470-11471.

7. Lee, Y.; Mitzi, D. B.; Barnes, P. W.; and Vogt, T.; (2003) Pressure-Induced Phase Transitions and Templating Effect in Three-Dimensional Organic-Inorganic Hybrid Perovskites. *Phys. Rev. B*, 68, 020103(R).

8. Lee, Y.; Hriljac, J. A.; Studer, A.; and Vogt, T.; (in press) Anisotropic Compression of Edingtonite and Thomsonite to 6 GPa at Room Temperature. *Phys. Chem. Mineral.*

9. Lee, Y.; Hriljac, J. A.; Kim, S.-J.; Hanson, J. C.; and Vogt, T.; (2003) Pressure-induced Hydration at 0.6 GPa in a Synthetic Gallosilicate Zeolite. *J. Am. Chem. Soc.* 125: 6036-6037.

Magazines

Parise, J. B.; Lee, Y.; Hanson, J. C.; Vogt, T.; Hriljac, J. A.; Rietveld Refinement Using Time-Resolved Synchrotron X-ray Powder Diffraction Data To Study Transformations in Zeolites. *International Union of Crystallography Newsletter*, No. 29, p. 7-11, June 2003.

Patents

Pressure Induced Swelling in Microporous Materials (Docket #369-171), Vogt, T.; Hriljac, J. A.; Lee, Y.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2002 | \$79,000 |
| FY 2003 | \$82,600 |
| FY 2004 (budgeted) | \$54,900 |

Genomic SELEX to Study Protein DNA/RNA Interactions in *Ralstonia metallidurans* CH34 Regulating Heavy Metal Homeostasis and Resistance

Daniel van der Lelie

02-084A

PURPOSE:

The aim of this proposal is to use a SELEX (Systematic Evolution of Ligands by Exponential enrichment) approach to establish a protein-nucleic acid linkage map for heavy metal resistance and homeostasis in *Ralstonia metallidurans* CH34.

APPROACH:

The SELEX approach, which was carried out in collaboration with S. Taghavi and J. Flanagan, involves the following logical steps: selection of key-regulator genes; cloning, over-expression and purification of proteins; strategy for the generation of random DNA/RNA fragments; SELEX enrichment of nucleotide fragments interacting with regulatory protein.

TECHNICAL PROGRESS AND RESULTS:

Phylogenetic analysis of heavy metal resistance regulators. After a BLAST search of the nearly completed sequenced genome of *Ralstonia metallidurans* CH34, 10 PbrR/MerR like regulators were identified. These regulators could, based on sequence similarity and functional linkage to structural resistance proteins, be divided into four major groups. Members of the different groups were chosen for cloning in protein over-expression vectors. At present the work concentrates on members of the MerR

family (*merR* genes from the contigs 691, 663 and Tn4378), where identical regulators were found to be involved in the regulation of three mercury resistance genes and on the PbrR-like regulator from contig 710. The *pbrR*-like gene on contig 710 was not physically linked to any structural heavy metal resistance gene. Therefore, SELEX is an ideal approach to identify the PbrR710 regulated functions that are located physically distant on the chromosome.

A total of 10 *merR*-like and *pbrR*-like regulators were cloned as His-tag fusions in pET28 and pET30 and checked for over-expression. One protein, referred to as MerR663, was purified and checked for its stability. We chose this protein, as we were able to produce it in high, soluble quantities. On the other hand, we had problems with purifying some as the MerR like proteins, such as PbrR710, as they tended to form insoluble complexes upon over expression in *Escherichia coli*. Subsequently, we made a MerR663 affinity column that should specifically retain DNA fragments recognized by MerR663. At this moment we have started enrichments of DNA fragments using two approaches: the classical SELEX approach using random 39-mer synthesized DNA fragments and the Genome Signature Tag approach where we generate 21 base pair DNA fragments that flank the region of DNA that is recognized by the MerR protein.

Random DNA fragments for SELEX enrichments. A library of random DNA fragments for SELEX enrichment was constructed based on the following principles (Fig. 1):

- random 40bp DNA fragment, flanked by well-defined ends:
 - One end allows conversion into RNA using the T7 promoter

- RNA can be converted into ss-DNA
- ds-DNA is obtained by simple PCR amplification

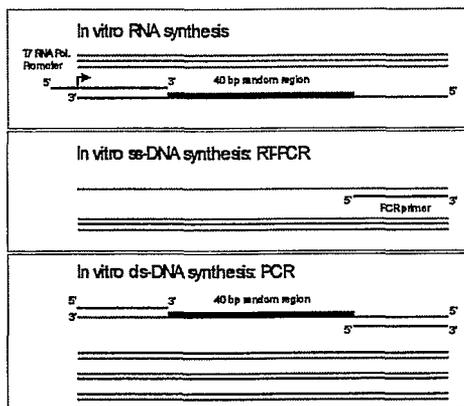


Figure 1. Strategies for generating Random DNA/RNA fragments for SELEX enrichment.

Reorientation of the work. Although regulatory pathways are one of the goals of DOE's Genomes to Life (GTL) program, our strategy is not suitable for high throughput identification of protein-nucleotide interactions as is solicited by DOE. Therefore, part of the effort of this LDRD was reoriented towards the analysis of the composition and functioning of microbial communities; especially microbial communities associated with contaminated sites, which is also a goal of DOE's GTL program. The earlier mentioned Genome Sequence Tag Technology was further developed, and we also developed the singular point GST technology (SP-GST) that generates tags from specific sequences in the genome. An example of this is the 16S rRNA gene based SP-GST, that generates 21 base pair DNA fragments that are linked to the 16S rRNA genes of microorganisms. The fragments can be used to obtain a detailed overview of the composition of complex microbial communities.

SPECIFIC ACCOMPLISHMENTS:

Dunn, J. J.; McCorkle, S. R.; Praissman, L. A.; Hind, G.; van der Lelie, D.; Bahou, W. F.; Gnatenko, D. V.; and Krause, M. K. Genomic signature tags (GSTs): A new system for profiling genomic DNA. *Genomic Res.* 12, 1756-1765 (2002).

Mergeay, M.; Monchy, S.; Vallaey, T.; Auquier, V.; Benotmane, A.; Bertin, P.; Dunn, J.; Taghavi, S.; van der Lelie, D.; and Wattiez, R. *Ralstonia metallidurans*, a bacterium specifically adapted to toxic metals: towards a tentative catalogue of metal-responsive genes. *FEMS Microbial Rev.* 27(2-3), 385-410 (2003).

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$163,972 |
| FY 2003 | \$170,900 |
| FY 2004 (budgeted) | \$165,000 |

Lead Resistance in *Ralstonia metallidurans* CH34

Safiyh Taghavi

02-084B

D. van der Lelie

PURPOSE:

The purpose of this project is to further elucidate the functioning of the *pbr*TRABCD lead resistance operon of *Ralstonia metallidurans* CH34 and to determine the role and interactions of the different lead resistance proteins.

APPROACH:

In order to study the role of the different components of the *pbr*TRABCD lead resistance operon of *Ralstonia metallidurans* CH34, the operon was cloned and subsequently a library of different knock-out mutants was constructed. Sequence analysis was used to identify different *pbr* mutants.

To study the functioning of the *pbr* proteins, we cloned them in a pET protein expression system. This work was carried out in collaboration with J. Flanagan.

As part of the effort to sequence and analyse the genome of *Ralstonia metallidurans* CH34, we identified and studied different PbrR and MerR like regulators. Work on the *Ralstonia metallidurans* CH34 genome is done in collaboration with M. Mergeay, Center for Studies of Nuclear Energy, Mol, Belgium.

LuxCDABE fusions were constructed to study the role of PbrR-like regulators. Biosensor applications are part of a collaboration between BNL and Vito, the Flemish Institute for Technological Research.

TECHNICAL PROGRESS AND RESULTS:

Isolation of *pbr* mutants. Using the EZ::Tn(Km2) *in vitro* transposition system we constructed a library of *pbr*::Tn(Km2) mutants. A total of 400 mutants were obtained that were all analyzed by restriction digestion. The presumed positions of the transposon insertions were confirmed by sequence analysis. With the exception of the *pbrR* gene, we obtained mutants in all other genes of the *pbr* operon. These mutants were subsequently analyzed for their lead resistance phenotype. To our surprise, *pbrB* was the only gene indispensable for lead resistance. As most of the other *pbr* genes have chromosomal counterparts, it is hypothesized that the activities of the other genes can be complemented. This is presently being examined with the help of quantitative polymerase chain reaction (PCR). Our hypothesis is that the transcription of chromosomal genes will go up when their plasmid counterpart has been inactivated.

Further analysis of the PbrB protein showed that it is a phosphatase. Our working hypothesis is that PbrB liberates a phosphate from an organic compound, such as a sugar, and that this phosphate is used to precipitate the lead that is exported by the PbrA lead efflux ATPase.

Phylogenetic analysis of PbrR-like regulators. After a BLAST search of the nearly completed sequenced genome of *Ralstonia metallidurans* CH34, 10 PbrR/MerR like regulators were identified. These regulators could, based on sequence similarity and functional linkage to structural resistance proteins, be divided into four major groups.

Reorientation of work. Based on our past experience (at Vito, Belgium) with the construction, testing and evaluation of bacterial biosensors and the interest for these sensors in the scientific community, we decided to reorient part of our efforts to the application of bacterial biosensors to evaluate the bioavailability of heavy metals in environmental samples. We successfully demonstrated the possibilities of these biosensors by evaluating heavy metal bioavailability in sludge from the NY/NJ harbor. We also used our biosensors to link metal bioavailability with plant uptake. This work was part of a collaboration with the University of Delaware.

Our Work Has Been The Basis Of A Much Better Understanding Of Lead Resistance In *Ralstonia Metallidurans* Ch34.

SPECIFIC ACCOMPLISHMENTS:

Based on the experience with the *lux*-based heavy metal biosensors, we successfully applied for a project entitled "The Impact of Surface Precipitation on Sequestration and Bioavailability of Metals in Soils."

Publications:

Geebelen, W.; Adriano, D. C.; van der Lelie, D.; Mench, M.; Carleer, R.; Clijsters, H.; and Vangronsveld, J. Selected bioavailability assays to test the efficacy of amendment-induced immobilization of lead in soils. *Plant and Soil* 249, 217–228 (2003).

Mergeay, M.; Monchy, S.; Vallaeys, T.; Auquier, V.; Benotmane, A.; Bertin, P.; Dunn, J.; Taghavi, S.; van der Lelie, D.; and Wattiez, R. *Ralstonia metallidurans*, a bacterium specifically adapted to toxic metals: towards a tentative catalogue of metal-responsive genes. *FEMS Microbial Rev.* 27(2-3), 385-410 (2003).

Adriaensen, K.; van der Lelie, D.; Van Laere, A.; Vangronsveld, J.; and Colpaert, J. V. A zinc adapted fungus protects pines from zinc stress. *New Phytologist* (accepted).

Vassilev, A.; Schwitzguébel, J. -P.; van der Lelie, D.; and Vangronsveld, J. The use of plants for remediation of metal contaminated soils. *Scientific World* (accepted).

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$161,408 |
| FY 2003 | \$170,100 |
| FY 2004 (budgeted) | \$170,000 |

Design of a *Ralstonia metallidurans* Two-Hybrid Protein System for Studying Signaling Pathways Regulating Heavy Metal Homeostasis and Resistance

Safiyh Taghavi

02-085

PURPOSE:

This proposal aims at developing 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.

APPROACH:

Construct a suitable Two-Hybrid protein system for the construction and screening of libraries from *Ralstonia metallidurans* CH34.

TECHNICAL PROGRESS AND RESULTS:

The following major research accomplishments were obtained for this LDRD project: A new vector was constructed and evaluated for Two-Hybrid protein interactions. Using this system we demonstrated the interaction between two regulatory proteins of the *cnr* cobalt-nickel resistance system of *Ralstonia metallidurans* CH34. During this work we also came to the conclusion that the system was unsuitable for the high throughput construction of protein-protein interaction maps. Something for which better alternatives were available, such as protein-protein micro arrays. Therefore, we decided to stop this line of research and to cancel the third year of this LDRD project.

It turned out that *Ralstonia metallidurans* proteins are quite poorly expressed in *Escherichia coli*. This prompted us to construct an expression system, based on the XylS-Pm regulon, for protein expression in *Ralstonia metallidurans*. In total we constructed seven different vectors that vary in their affinity tag and multiple cloning site. We subsequently cloned five different heavy metal resistance genes from *Ralstonia metallidurans* CH34 in these vectors, in order to study their expression and solubility. The genes were *cnrA*, a part of the three components involved in Cobalt and Nickel resistances; *czcD*, a cation diffusion facilitator involved in Cadmium, Zinc and Cobalt resistances and three genes from the *pbr*, Lead resistance operon (*pbrA*, *pbrT* and *pbrD*). The constructs were introduced in the strain CH34 and the strain AE104 where they will be screened for heavy metal resistance phenotypes as well as protein expression.

SPECIFIC ACCOMPLISHMENTS:

Publications:

Lodewyckx, C.; Vangronsveld, J.; Porteous, F.; Moore, E. R. B.; Taghavi S.; and van der Lelie, D. Endophytic bacteria and their potential applications. *Critical Rev. Plant. Sci.* 21, 583-606 (2002).

Mergeay, M.; Monchy, S.; Vallaey, T.; Auquier, V.; Benotmane, A.; Bertin, P.; Dunn, J.; Taghavi, S.; van der Lelie, D.; and Wattiez, R. *Ralstonia metallidurans*, a bacterium specifically adapted to toxic metals: towards a tentative catalogue of metal-responsive genes. *FEMS Microbial Rev.* 27(2-3), 385-410 (2003).

Snellinx, Z.; Taghavi, S.; Vangronsveld, J.; and van der Lelie, D. Microbial consortia

that degrade 2,4-DNT by interspecies metabolism: Isolation and characterization. *Biodegradation* 14, 19-29 (2003).

Barac, T.; Borremans, B.; Provoost, A.; Oeyen, L.; Colpaert, J. V.; Vangronsveld, J.; Taghavi, S.; and van der Lelie, D. Engineered endophytic bacteria improve phytoremediation of water-soluble volatile organic pollutants. *Nature Bio. Technol.* (submitted).

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$168,188 |
| FY 2003 | \$173,900 |

Ultrafast X-ray Science

Steve Dierker

02-086

B. Sheehy

C.-C. Kao

PURPOSE:

Developing new X-ray sources and techniques and making them available to the user community is an important part of the NSLS mission. In recent years, some of the most important developments in the field have concerned time-resolved studies using X-rays. These promise to open new frontiers in chemical dynamics, material science, and biology, as simultaneous resolution at both molecular time scales and atomic spatial scales becomes a reality. New sources are capable of producing subpicosecond bursts of X-rays, and new techniques are being used to obtain subpicosecond resolution using synchrotron sources. Existing resources at the NSLS can be adapted for these purposes, and the purpose of this project is to carry this development forward.

APPROACH:

The Source Development Laboratory (SDL) contains a Ti:Sapphire laser system capable of producing 0.5 Terawatt peak power pulses in the infrared (800 nm wavelength). Such a source is capable of producing intensities between 10^{17} and 10^{18} W/cm² and so is an ideal candidate for a laser-driven plasma X-ray source. In such a source, the laser is focused on a metal target, forming an ultradense plasma. Energetic electrons are produced and decelerated rapidly, producing continuous bremsstrahlung radiation to energies on the order of 10 keV. Electrons penetrating the surface also eject core electrons, producing prompt K_{α} and K_{β} lines as well. In order to achieve this, certain improvements have to be made to the laser.

The contrast – the ratio between the main laser pulse and a precursor pulse which is due to the amplification method – must be brought above 10^6 . Some of this will be done with improvements in the amplifier design. A pulse cleaner must also be implemented after the first amplifier. We will also experiment with using the laser's second harmonic for the X-ray generation since, in addition to improving the contrast, this may improve the efficiency of the device.

On the synchrotron rings, we will expand the program in time-resolved experiments by developing ultrafast detection methods. This will include optical pump – X-ray probe experiments.

TECHNICAL PROGRESS AND RESULTS:

The postdoctoral researcher approved for this project has been hired. Yuzhen Shen joined the staff in October 2002.

In the ultrafast X-ray source project, design work on the laser modifications has been done, and construction was completed in June 2003. A new regenerative amplifier design was implemented, a second amplifier brought into service, and dual pulse cleaners developed. A contrast between 10^6 - 10^7 has been achieved, and focal spot size measurements indicate that we will be able to reach a peak intensity of 10^{17} W/cm². The necessary modifications to the laser room have been completed, and a new optical table installed. Beam transport to the source area and the optical layout for the source has been completed and tested. The moving wire source has been constructed, and software for its operation is being developed. A shielding design has been made, and construction of the lead housing for shielding hard x-rays has been completed. Our collaboration continues

with Professor Christoph Rose-Petruck of Brown University, who has assisted us in the target fabrication and other source development issues. We anticipate that the first X-rays will be made before the end of 2003.

A laser has been purchased (from NSLS capital funds) to support the optical pump – X-ray probe program on the synchrotron rings. A design was developed with the vendor that will permit the laser to operate initially in the ultraviolet, for a currently planned program of nanosecond experiments. The laser can subsequently be

converted to a pump laser for an ultrafast system for future experiments. The X6B beamline is currently being refitted to accommodate the nanosecond experiments.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$100,018 |
| FY 2003 | \$105,000 |
| FY 2004 (budgeted) | \$105,000 |

X-ray Photon Correlation Spectroscopy Studies of Nanostructured Block Copolymers

Steve Dierker

02-088

PURPOSE:

The objective of the proposed research is to use the technique of X-ray Photon Correlation Spectroscopy (XPCS) to study the short length scale dynamics of both binary homopolymer blends and also nanostructured block copolymers. The goal of the study is to provide an experimental base from which a theoretical understanding of the short wavelength dynamics might be constructed. As a prelude to the block copolymer studies, the previously unexplored 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. In the block copolymers, the previously unexplored dynamics in the unentangled regime, as well as the little explored behavior near the critical wave vector for microphase separation will be studied.

APPROACH:

On a macroscopic level, the miscibility, phase behavior, and rheology of polymers have been extensively studied. The static properties of both binary polymer blends and block copolymers have been investigated by a variety of different scattering techniques, including light scattering, small angle x-ray scattering, and mainly small angle neutron scattering. The dynamic properties, on the other hand, are relatively less well explored, especially in nanostructured block copolymers, despite their obvious

importance in understanding the microscopic origins of their tremendously variable macroscopic rheology. Essentially all previous experiments have been limited to studying the long wavelength dynamics of polymers, which provide little if any information as to how the dynamics evolve as one probes to shorter length scales, comparable to the nanostructure of the polymer. The objective of this research is to use XPCS to make experimental results on the short length scale dynamics of polymers available for the first time. Since it utilizes a coherent x-ray beam, the XPCS technique necessitates a high brilliance x-ray source. Coherence and high brilliance are distinguishing characteristics of the planned NSLS Upgrade and this project contributes expertise and scientific justification for the NSLS Upgrade.

TECHNICAL PROGRESS AND RESULTS:

Sample cells for the polymer XPCS experiments were fabricated and a series of Small Angle X-ray Scattering (SAXS) and XPCS measurements on homopolymer mixtures of polystyrene and polybutadiene were performed in several synchrotron runs at the NSLS and at the APS. Data were collected on the static and dynamic critical behavior at the order-disorder transition from a homogeneous mixture to a macroscopically separated phase.

The quality of data collected in these experiments has been limited by the detector. Previous work has utilized a high speed x-ray sensitive area detector to record movies of the fluctuating speckle pattern which are recorded to computer hard disk for later analysis. Despite being high speed, the fastest correlation times measurable are limited by the frame rate of the charge-coupled device (CCD) to several hundred msec or longer. At the same time, the

amount of data is limited by the CCD readout hardware.

In order to overcome both of these limitations, we are developing a 2D gas detector which has high quantum efficiency, high speed readout, and high position resolution. This is being done in collaboration with Graham Smith in the Instrumentation Division. We have developed and refined the detector through several prototypes. We are also developing a custom electronic readout circuit for the detector to further enhance the readout rate and position resolution by adapting a similar circuit developed by Peter Siddons in the NLSL for another gas detector developed there for high throughput powder diffraction.

The new detector is expected to be ready to be used in experiments in the coming year. These previous experiments on homopolymer blends will be extended to shorter correlation times and will be followed by a series of experiments in a block copolymer blend.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2002 | \$ 90,212 |
| FY 2003 | \$105,000 |
| FY 2004 (budgeted) | \$105,000 |

Fine Grain Gas and Silicon Detectors for Future Experiments in Nuclear Physics at High Energies

*Craig Woody
T. Hallman*

02-091

PURPOSE:

The purpose of this work is to investigate several new technologies, which could be of great importance in the future of nuclear physics experiments at high energies. These are high-resolution gas tracking devices based on so-called micropattern detectors, and high granularity silicon pixel detectors. The objective is to determine whether any of these new technologies could be used for the next generation of detectors at RHIC (Relativistic Heavy Ion Collider) that would enhance their physics capabilities or improve their performance in future years. If these technologies prove to be useful at RHIC, there would be significant scientific benefit to the RHIC program and additional funding to continue this project could be expected from DOE Nuclear Physics.

APPROACH:

The physics program at RHIC has already provided many interesting and exciting new discoveries. While stopping just short of claiming the discovery of the Quark Gluon Plasma, it has clearly demonstrated the formation of extremely hot, dense nuclear matter with unique properties in relativistic heavy ion collisions, and has opened the door to the exploration of polarized proton collisions at very high energies. The current suite of RHIC detectors has proven to be very effective in studying these types of collisions, but there are new phenomena, which require further enhanced detector

capabilities. These include the measurement of low mass dilepton pairs and vector mesons, and a detailed systematic study of heavy quark production in both heavy ion and polarized proton collisions. To study these phenomena, new detector technologies are required. Two such technologies are high precision tracking detectors capable of identifying and rejecting Dalitz pairs and photon conversions in high multiplicity heavy ion collisions, and very high-resolution vertex detectors capable of resolving secondary vertices at the level of a few tens of microns. This project investigated the use of micropattern detectors for high-resolution particle tracking and silicon pixel detector for vertex finding. Specifically, we have studied the properties of Gas Electron Multipliers (GEM) and MicroMega detectors for use in a fast, compact Time Projection Chamber (TPC) and Hadron Blind Detector (HBD) which would be used as a device to reject Dalitz pairs and conversions, and both hybrid and active silicon pixel detectors as possible high resolution vertex detectors. This work was carried out in collaboration with members from both the PHENIX (Pioneering High Energy Nuclear Interaction Experiment) and STAR (Solenoidal Tracker) collaborations.

TECHNICAL PROGRESS AND RESULTS:

During FY 2003, numerous micro pattern GEM detectors were tested for use in a TPC and/or HBD configuration. GEM foils were obtained from CERN as well as from a new commercial supplier (3M Microinterconnect System Division, Austin, TX). The foils were assembled into three stage GEM detectors and tested with various gases and electrode configurations. For testing the TPC configuration, a drift cell, shown in Figure 1, was constructed which allowed the

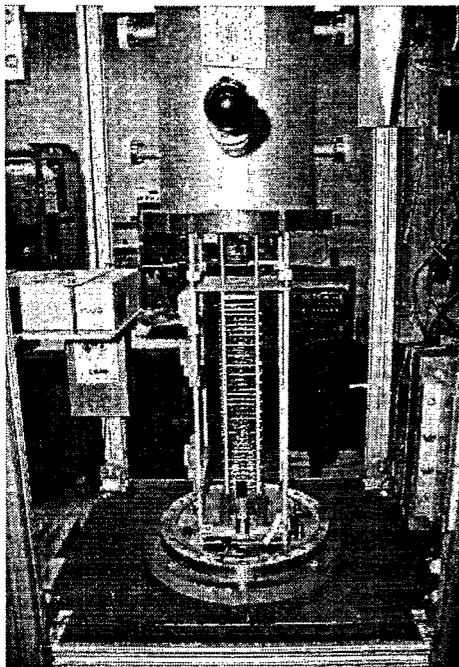


Figure 1. TPC drift cell with a three stage GEM detector at the bottom of the stack.

measurement of drift velocities and diffusion parameters of various gases.

Measurements were carried out with the drift cell for a number of gases that might be used in a fast TPC detector. Figure 2 shows the results of some of the measurements of the charge spread distribution on the readout plane of the GEM detector for a gas mixture of Ar(95%)/CF₄(5%). The width of the charge spread was determined to be ~ 1.7 mm, which was consistent with the diffusion expected over the approximately 30 cm drift used for this measurement.

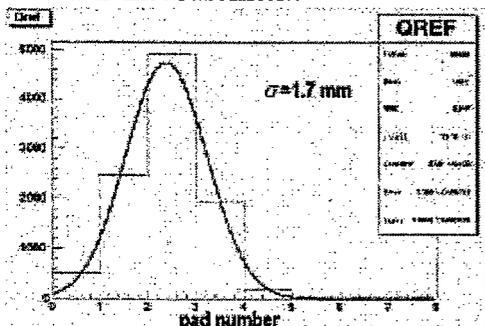


Figure 2. Charge spread distribution at the readout plane of the GEM detector after ~ 30 cm drift in Ar(95%)/CF₄(5%)

Numerous tests were also carried out comparing the 3M GEM foils with the foils produced at CERN. Differences were found in both the physical composition and the performance of these foils. While the 3M foils showed slightly higher gain for the same voltage and electrode configuration, as shown in Figure 3, the CERN foils showed better long-term stability. This may have been due to the different type of kapton used to produce the foils, or possibly the process of cleaning or treating the foils after they are produced. These issues are still under investigation and discussions with both CERN and 3M are continuing.

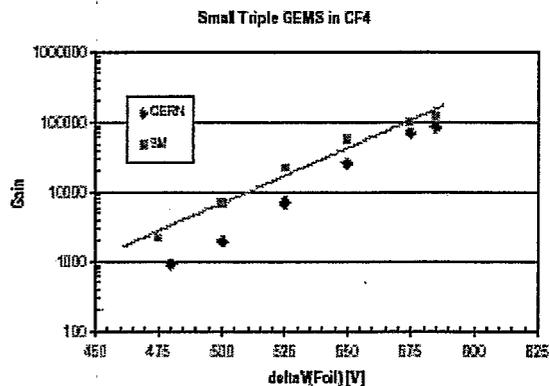


Figure 3. Comparison of the gain curves for three stage GEM detectors comprised of 3M vs. CERN foils in pure CF₄.

During the final year of this LDRD, the effort on the silicon pixel detectors was largely taken over by other groups of the PHENIX and STAR collaborations, which allowed more resources to be devoted to the gas detector work. STAR is also carrying out R&D at other institutions on the design of an active silicon pixel detector as part of their future upgrade program.

SPECIFIC ACCOMPLISHMENTS:

Accomplishments included the complete construction of the TPC drift cell and carry out measurements of critical parameters for a fast, compact TPC with a micropattern

detector readout. These included measurements of drift velocities, diffusion parameters, charge spread distributions, gain curves and gain stability measurements with several types of GEM detectors. Another specific accomplishment was a detailed comparison of GEM foils produced by two different manufacturers and an evaluation of how these foils would perform in an actual detector.

These efforts have been highly successful and have resulted in a formal proposal from the PHENIX collaboration to the DOE for the construction of a new silicon vertex and tracking detector.

It should also be noted that this LDRD has led to new funding from the DOE to continue this work as a part of the RHIC detector upgrade programs for both PHENIX and STAR.

Papers presented at meetings leading to publications in referred journals:

A Study of GEM Characteristics for Application in a MicroTPC, B.Yu, et.al., paper published in the IEEE Transactions on Nuclear Science, NS 50, Vol. 4 (2003) pp. 836-841.

Talks given at Conferences or Workshops:

A Fast, Compact TPC with GEM Readout for Tracking and Electron Identification for RHIC, C. Woody, invited talk given at the Linear Collider Workshop, Berkeley, CA, October 18, 2003.

A Fast, Compact TPC with GEM Readout for Tracking and Electron Identification for RHIC, C. Woody, talk given at the Workshop on Micropattern Detectors for Time Projection Chambers at the 2003 IEEE Nuclear Science Symposium and Medical Imaging Conference, Portland, Oregon, October 20, 2003.

Compact TPC Readout in the PHENIX Experiment, C -Y. CHI, talk given at the Workshop on Micropattern Detectors for Time Projection Chambers at the 2003 IEEE Nuclear Science Symposium and Medical Imaging Conference, Portland, Oregon, October 20, 2003.

LDRD FUNDING:

| | |
|---------|-----------|
| FY 2002 | \$ 99,511 |
| FY 2003 | \$100,000 |

High-Brightness, High-Power Electron Beams

Ilan Ben-Zvi

03-004

PURPOSE:

The objective of this work is to develop bright and high power electron beams from photoinjector electron sources. This is done through the development of continuous wave (CW) photoinjectors and critical subcomponents for the photoinjectors. Getting a high brightness and high power electron beam is a risky, cutting edge R&D, but the payoff could be high in enabling new radiation sources such as x-ray free electron lasers (FELs) and Photoinjected Energy Recovery Linacs, electron cooling for RHIC and high-power FELs for defense applications.

APPROACH:

The PI, in collaboration with Triveni Srinivasan-Rao, undertook to carry out the development of superconducting laser photocathode RF guns and the associated laser illumination system. In a recent development, an opportunity presented itself to broaden the initial approach of niobium metal as the photocathode material to cover also a multi-alkaline cathode in a superconducting gun.

TECHNICAL PROGRESS AND RESULTS:

In FY 2003 we made progress on the preparation of the superconducting photoinjector and its test system. Figure 1 shows the superconducting, all-niobium photoinjector that we are using. The approach in this particular gun is to use the back of the gun as the photocathode. The

advantage of this approach is a robust, long-lived cathode which is suitable for applications such as a self-amplified spontaneous emission (SASE) (or high-gain harmonic generation [HG] X-ray FEL. The disadvantage is the relatively low quantum efficiency. This issue will be addressed later on.

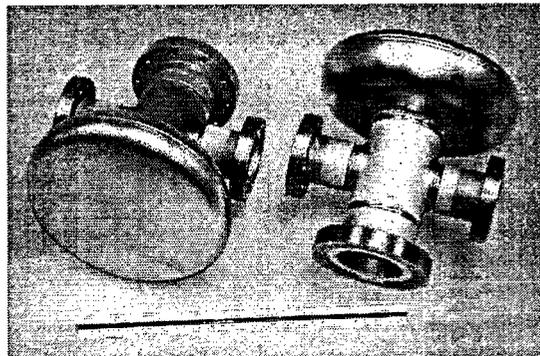


Figure 1. Superconducting photoinjector units.

The gun and its cryostat have been assembled with a beam-line designed to introduce the laser power in and collect the electron beam into a Faraday cup and measured. The cryostat and beam-line assembly can be seen in Figure 2.

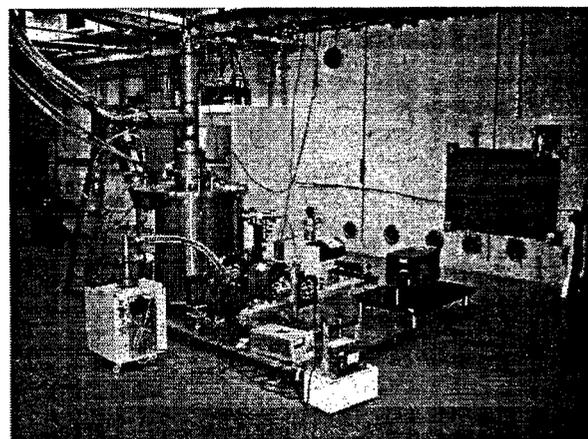


Figure 2. Cryostat and beam line assembly.

The low level RF system has been designed, built, and is being tested. The gun cavity, before chemical cleaning, has been cooled down to 4K. The frequency and the Q of the superconducting cavity have been measured.

The Q measured 10^7 at 4K, presumably limited by the dirty surface. The cavity is now at Jefferson Laboratory for chemical cleaning. On the laser item, the plan is to produce a ~10 MHz 5 W laser beam that is applicable for both 532 nm radiation that can be used for antimonide cathodes as well as 266 nm radiation for the Nb gun. This is shown schematically in Figure 3. The concept is to take the fundamental 1064 nm radiation from our Time Bandwidth laser and inject it into a ring resonator cavity. In the resonator the green (532nm) will be generated and trapped to build up power, and it will also be used to generate 266 nm light. The 266 nm light will pass out of the ring resonator into a simple linear resonator cavity with an Acousto-optic (AO) modulator inside. The AO modulator will then kick out every 8th pulse at approximately 10 MHz. In a similar fashion the 532 nm light from this system could be ejected at 10 MHz by replacing the beta-BaB2O4 (BBO) crystal with the AO modulator. The laser has been characterized, and the transport system is being built. A resonant multi-pass cavity with 8 passes was preliminary designed.

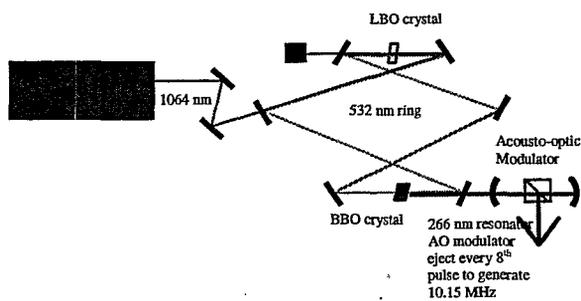


Figure 3. Optical harmonic generating resonator.

As mentioned above, the quantum efficiency of niobium metal is good for certain applications such as X-ray FELs, but not for

high-current applications such as electron cooling. There is a growing interest in the community of photoinjectors to produce a superconducting photoinjector capable of ampere-class current. That would require inserting a multi-alkaline cathode into the superconducting RF gun. We plan to take advantage of a photocathode deposition system at BNL to test some ideas as to how to introduce a multi-alkaline photocathode into a superconducting cavity and measure the effect of possible migration of alkaline contamination into the cavity walls.

SPECIFIC ACCOMPLISHMENTS:

1. J. Sekutowicz, A. Bogacz, M. Ferrario, I. Ben-Zvi, P. Colestock, D. Douglas, P. Kneisel, W.-D. Möller, D. Proch, J. Rose, J. B. Rosenzweig, L. Serafini, S. Simrock, T. Srinivasan-Rao, G. Williams. CW Energy Recovery Operation of XFEL, Proceeding 2003 Superconducting RF Workshop, September 8-12, Travemunde, Germany.
2. T. Srinivasan-Rao, I. Ben-Zvi, A. Burrill, G. Citver, A. Hershcovitch, D. Pate, A. Reuter, J. Scaduto, Q. Zhao, Y. Zhao, H. Bluem, M. Cole, A. Favale, J. W. Rathke, T.J. Schultheiss, J. Delayen, P. Kneisel, Design, Construction and Status of an All Niobium Superconducting Photoinjector at BNL, Proceedings, 2003 Particle Accelerator Conference, May 12-16, Portland Oregon.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$150,000 |
| FY 2004 (budgeted) | \$192,000 |

Feasibility Study of the Optical Stochastic Cooling with a CO₂ Laser

Vitaly Yakimenko

03-006

PURPOSE:

We intend to develop and test an optical amplifier that would be suitable for the optical stochastic cooling (OSC) at RHIC. Our calculations demonstrate that OSC operated at a 12 micron wavelength can effectively improve RHIC performance. OSC can successfully replace microwave stochastic cooling (SC) that is currently proposed for RHIC and experiments are planned for the spring of 2004. OSC has the potential to affect whole beam which is in contrast to SC which deals with a small percentage of the beam. OSC is complimentary to the electron cooling (EC) - another RHIC cooling project. EC is more effective for the particles with small amplitudes, while OSC works faster at large amplitudes. Thus, the addition of the OSC to the EC would dramatically reduce requirements of the electron current in the EC project.

APPROACH:

Using an optical parametric amplifier (OPA) pumped by the second harmonic of the Accelerator Test Facility (ATF) high power pulsed CO₂ laser, we intend to characterize the amplification of a CW CO₂ laser at 9 microns. Demonstration of the successful amplification using this OPA will allow us to extrapolate the performance expected under the conditions required for the optical stochastic cooling of RHIC. Possible experiments using the output of the Jefferson Laboratory (JLAB) Free Electron Laser (FEL) as a pump source for OPA

would allow testing an optical amplifier at full power load are planned for the second year of LDRD.

TECHNICAL PROGRESS AND RESULTS:

A new approach was chosen for the optical amplifier consisting of replacing a 12-meter long gas laser-based amplifier with a 3.5 cm long nonlinear crystal. This makes the project extremely appealing for the near-term realization at RHIC. Extensive calculations of the OPA for OSC were performed. A test stand was designed and assembled to verify performance of the OPA in the low repetition (low thermal load) mode of operation. Full power testing with the "RHIC" duty factor utilizing the output of the JLAB FEL is in the planning stage.

We started designing the CO₂ based pump source. It consisted of a mode-locked CO₂ based oscillator at 10 MHz and commercially available CW CO₂ welding lasers. Experimental testing of the mode locked CO₂ based oscillator is the last item in the optical amplifier part of the OSC project that needs verification.

SPECIFIC ACCOMPLISHMENTS:

Publication:

Optical Stochastic Cooling for RHIC using Optical Parametric Amplification, M. Babzien, I. Ben-Zvi, I. Pavlishin, I. V. Pogorelsky, V. E. Yakimenko, A. A. Zholents, and M. S. Zolotarev, submitted to Phys. Rev. ST

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$110,000 |
| FY 2004 (budgeted) | \$126,400 |

Proposal for Niobium/Tin Superconducting Magnet

Erich Willen

03-013

PURPOSE:

The BNL Magnet Division built the superconducting helical magnets for the Spin Program at RHIC using a new method of magnet construction. This new method used slots machined into a thick-walled cylinder to contain the ductile NbTi superconductor. Because this approach does not significantly strain the superconductor, it holds promise for building magnets with the brittle Nb₃Sn superconductor. If successful, this would allow higher magnetic fields to be obtained in accelerator magnets and would open the door to many applications, from Light Source undulators, to improved performance in a Muon Collider, to upgrades for the new Large Hadron Collider at CERN.

APPROACH:

Building on the experience gained in the Spin magnet program, the Magnet Division would extend the construction techniques developed there to the use of pre-reacted Nb₃Sn. Those magnet coils were made by placing a small diameter NbTi cable into slots milled into thick-walled aluminum cylinders. This technique does not strain the cable during construction and the slots control the magnetic forces during magnet excitation. That is precisely what is needed for the Nb₃Sn superconductor, which becomes brittle after reaction. Our plan is to make two concentric coils with 7 and 9 slots respectively. We used the small amount of ITER (International Thermonuclear Experimental Reactor) material already available at BNL for an early start on the construction of a coil, and will use new material and supplies to extend this work to the construction and test of two coils and a short but complete magnet.

TECHNICAL PROGRESS AND RESULTS:

Superconductor wire was received from two vendors and is being cabled, reacted and insulated. Prepreg materials ("prepreg" is jargon for fiberglass cloth filled with a B-stage epoxy, which is cured after the parts are in place) for improved coil mechanical strength were received and are being tested. An outer slotted coil was designed, and a blank coil form was obtained. The existing inner slotted coil form was rewound several times with existing material. Ultrasonic seating of the cable into the slots was tested with good results. The best approach to routing and stabilizing the leads was determined. The test results were somewhat mixed but fairly reproducible: the windings have consistently reached about 75% of the expected short sample values. This is both good news and bad news: the reproducibility shows that pre-reacted material can be made into coils in a consistent way, but the reason for reaching only 75% of short sample is not yet understood.

When the new superconductor becomes available, the winding of the slots will resume and the ability to reach the expected short sample performance will be studied more extensively. All of the slots of the inner form will be filled with the superconductor and powered to study performance. If this is successful, the outer coil form will be machined and it too will be filled with superconductor and tested. Then the coils will be assembled together and tested as a completed magnet.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$147,800 |
| FY 2004 (budgeted) | \$157,300 |

Technology Development for Linear Collider Final Focus Quadrupoles with Small-Aperture High-Gradient Superconducting Coils

Brett Parker

03-014

PURPOSE:

The objective of this project is to see if it is possible to adapt BNL direct-wind magnet technology to make a superconducting final focus (FF) quadrupole, with five times smaller aperture but ten times higher gradient than previously achieved, that is appropriate for use at a future linear collider.

APPROACH:

BNL direct-wind technology was developed to make interaction region (IR) quadrupoles for the HERA Luminosity Upgrade (HERA-II) and is being adapted to making more complex (i.e. larger aperture but shorter length and greater number of coil layers) IR quadrupoles for the Beijing Electron Positron Collider (BEPC-II) Upgrade in Beijing, P.R. China. At the Snowmass 2001 meeting, the question was posed if our technology could be pushed in a different way to make small aperture but very high gradient magnets. The linear collider is a future high-priority high-energy physics project and this is an area where BNL is uniquely positioned to make an important contribution.

We developed a FF quadrupole concept that has a small radius coil wound from single strand wire placed inside a larger more conventional quadrupole made from the seven-strand cable used for BEPC-II. In this manner we avoid bending cable in too tight a radius while not making a coil with a large

number of turns and unacceptably large inductance. Our LDRD goal is to make a full length, 2 m, inner coil that could be quench tested in a vertical dewar. The LDRD work is complimentary to our BEPC-II large coil efforts yet there is much synergy between these two projects as noted below.

TECHNICAL PROGRESS AND RESULTS:

As previously reported we soon verified with a sequence of short test windings that it was indeed possible to wind single layer coils with the very tight bends on small diameter tubes; however, while this was a gratifying and necessary first step, it was not enough. The linear collider FF quadrupole requires ten such layers and our traditional (i.e. HERA-II) method of winding in independent single layers is not acceptable. Single layer leads are trapped in the inner pole regions and splicing together twenty such pairs of leads, in a region where there is little space, is a recipe for disaster.

The way we chose to mitigate this was to wind layers in "dual-layer" pairs so the leads can exit at coil ends, where there is room, rather than at poles. Dual-layer winding does mean having to nest and bond layers of wire above each other and this becomes very tricky where wires must cross over existing wires in order to connect turn N to turn N+1. Since the linear collider FF coils are 2 m long and the crossover can be done in about 25 mm, the project electrical engineer proposed simplifying production by making these transitions in the straight section, as shown in Figure 1, rather than in the ends (in conflict with making tight bends).

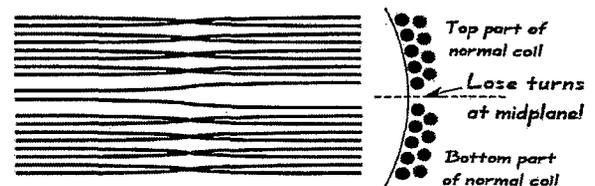


Figure 1: Normal Style Dual-Layer Schematic

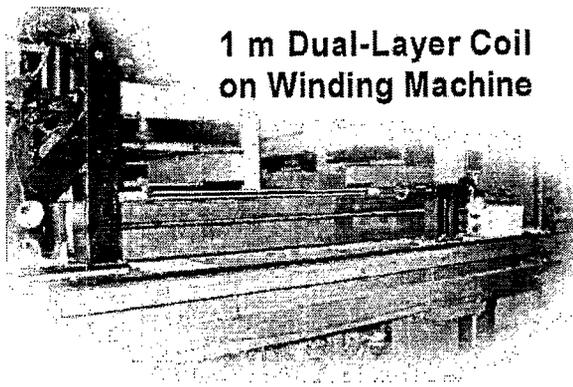


Figure 2: Normal Style Dual-Layer Coil Winding.

A series of short dual-layer test coils were wound culminating in a half-length, 1 m, coil shown in Figure 2. One result of winding the 1 m coil was to determine that a midpoint support was needed for winding a full-length coil. Pressure from the winding head causes the thin tube on which the coil is wound on to bow. Since tube deflection scales as the cube of the unsupported length, a 2 m long unsupported winding would deflect too much. A midpoint support was designed and installed in preparation for winding 2 m coils. However, in the time during which the midpoint support was being manufactured a significant theoretical advance in coil design has occurred.

A significant drawback of the winding compromise outlined in Figure 1 is that because each coil pack is wound in independent halves, the “jogs” in the straight section cause a loss of two turns in the bottom part of each dual-layer coil. This occurs right at the midplane where such a loss is most costly to magnetic efficiency. Coupled with the fact that the upper part of the dual-layer must have even fewer turns if it is to be nested, a large magnetic strength penalty occurs for this winding convenience.

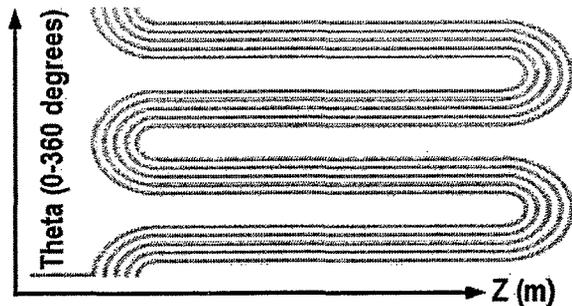


Figure 3: Serpentine Coil Winding concept

Figure 3 shows schematically a new “serpentine” topology for winding dual-layer coils we have recently invented that completely avoids this penalty. For a serpentine coil pattern all the turns for each pole of the bottom layer are laid down next to each other by letting the pattern wrap continuously around the tube. Note that an entire coil pack can be laid down in one step with no need for gaps at the coil midplanes.

The second part of the dual-layer serpentine coil (omitted for clarity in Figure 3) wraps around the tube in the opposite direction from and atop the first. It has opposite handedness and completes the quadrupole symmetry at coil ends. A nested serpentine still has to cross bottom layer turns at one end but it is possible to add a substrate wrap at the ends to aid winding as shown in Figure 4.



Figure 4: Dual-Layer Nested Serpentine Test Coil

We note also that with a serpentine winding it is possible to put a turn right on the coil midplane. The pattern shown in Figure 4 has an odd number of turns (which would be impossible with a traditional winding!) for an extra half turn per pole. Thus not only have we avoided losing turns, we can gain extra turns in the coil pattern and have finer

pattern control for fine tuning the magnetic field harmonics (i.e. by adding or subtracting half a turn).

The serpentine winding concept was invented to simplify the winding of BEPC-II coils. The concept was extended to do nested coils needed for making the linear collider FF quadrupoles.

Unfortunately the present midpoint support was designed with the assumption of winding one pole at a time and not continuously winding around the tube as the serpentine pattern does; so the midpoint support must be modified. When this is done we will attempt to wind and test the final 2 m long nested serpentine coil pattern.

Eventually we hope to secure additional funding to construct an outer coil and cryostat to combine with the 2 m inner coil resulting from our LDRD work. We would then have a realistic, full-scale prototype that could be useful in a second round of vibration measurements and testing.

SPECIFIC ACCOMPLISHMENTS:

The present work on nested serpentine coil windings is included in a record of invention report currently under preparation and is expected to be part of a patent application. In addition this work provides a basis for the superconducting FF magnet design for both the warm and cold options considered in the "Report of the United States Linear Collider Subgroup on Cost and Schedule" due out in early 2004.

Our LDRD plans were included in an early presentation, "Superconducting Final Focus Magnet Issues," contributed to Nanobeam 2002, the 26th Advanced ICFA Beam Dynamics Workshop on Nanometre Size Colliding Beams, September 2-6, 2002, Lausanne, Switzerland, that led to two invited talks.

The first is "The Compact Superconducting Final Focus Doublet Option," an invited talk presented at American Linear Collider Workshop, July 13-16, 2003, Cornell University, Ithaca, NY, USA.

Followed by "A Review of BNL Direct Wind Superconducting IR Magnet Experience," an invited talk presented at the 30th Advanced ICFA Beam Dynamics Workshop on High Luminosity e+e- Collisions, October 13-16, 2003, SLAC, Stanford, CA, USA and in the conference proceedings now under preparation.

As reported in "BNL FY04 Magnet Production and Measurement Activities," a talk presented at the NLC Collaboration Budget and Planning Meeting, October 28-29, Fermilab, Batavia, IL, USA, we have obtained initial NLC funding to study vibration issues in superconducting magnets using an existing RHIC magnet.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$125,000 |
| FY 2004 (budgeted) | \$130,000 |

Real-Time Detection and Multi-dimensional Characterization of Single Air-Borne Microorganism

Alla Zelenyuk

03-025

PURPOSE:

The purpose of this research project is to design, construct, and test a novel system capable of detecting and identifying single air-borne spores in real-time.

APPROACH:

Recent events have brought to the forefront the urgent need to develop a generation of instruments that can provide real-time warning of the presence of biohazards. For these instruments to be useful they must be extremely sensitive, specific, and operate remotely. Described below is a multidisciplinary program to design, construct, and test a novel Multi Dimensional - Single Particle Molecular Fingerprinter (MD-SPMF). We have brought together a team of scientists that includes: chemists and physicists to design, build, and test the hardware, a microbiologist to prepare the samples, a statistician to develop the software for real time data analysis, a computer scientist to produce a visualization interface to make it possible to assimilate the data in real-time, and a risk assessment expert.

The MD-SPMF is based on technology developed at BNL and implemented in the construction of Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS). The MD-SPMF is a single particle mass spectrometer that generates a detailed molecular fingerprint. MD-SPMF provides complete spectra for each

individual particle and is a zero background technique. Mass spectral biomarkers and MS-MS spectra, along with accurate particle size, particle shape and a proper library could in the future be used to detect and distinguish pathogens from harmless bacteria. MD-SPMF is an analytical tool that is remotely operable and requires no sample handling. It will be modified to detect and provide a very detailed signature that includes size, shape, molecular composition, and immunoassay, of a *single*, ambient bacterial cell or a *single* spore.

When complete, the proposed system will be able to detect and characterize a single spore in 1cm^3 of air in 1 second, providing a 5-dimensional (5-D) signature for each. The system utilizes an extremely efficient inlet that transmits nearly 100% of ambient particles forming a narrow particle beam. A dual optical detection is used to obtain accurate particle size and to start a timing clock that generates a trigger for the 4-color laser to provide information about particle shape. The IR pulse at 1064nm is used to evaporate the particle, pre-stored H_3O^+ ions produce molecular ions by chemical ionization, and the ions are mass analyzed. A second MS signature is produced through the process of MS-MS analysis.

We will take advantage of SPLAT-MS, our existing single particle laser ablation based instrument, to test concepts and components before the final multi dimensional single particle molecular fingerprinter is constructed. Methods for real-time data analysis, visualization, and risk assessment will be developed to produce a complete system that can be remotely operated to continuously monitor the environment, assess and transmit its findings.

TECHNICAL PROGRESS AND RESULTS:

1. The techniques to operate the particle mass spectrometer in the IR-UV operation mode was developed and tested with model specimens such as polystyrene beads and BG spores. Preliminary studies involving sample preparation and isolating single cells of *Pseudomonas fluorescens* have been completed. The spectra are much more reproducible and fragmentation is greatly reduced. SPLAT-MS was set up to determine characterization of microorganism using IR-UV evaporation/ ionization.

2. Experiments were started to examine the molecular fingerprints for various *Bacillus* and *Clostridium* species. This involved use of non-pathogenic bacteria to test and develop the analytical protocols. We prepared the vegetative cells and spores of the following non-pathogenic bacteria (i) aerobe: *Bacillus subtilis* as a surrogate for *B. anthracis*; (ii) anaerobe: *Clostridium* sp as a surrogate for *Clostridium botulinum* (botulism) and *C. tetani* (tetanus). Simulation of the matrix effect that would be normally encountered in the real world include: (i) spores and vegetative cells alone, (ii) a mixture of spores and vegetative cells, and (iii) spores and/or vegetative cells mixed with inert matrix such as talcum powder, sand, soil, or dust.

3. Hardware design and construction.

- Tested the optical system for shape and fluorescence. Software development for the pattern recognition included all dimensions and in particular the shape measurement.
- Continued to work on the classification Software with the Applied Mathematics and Statistics and Computer Sciences

Departments at Stony Brook by supporting graduate students in both departments.

- Statistical methods include neural networks, principal components analysis, metric development, and cluster, and analysis for classification of single-particle measurements. Focus on classification of particles according to their mass spectra and light scattering properties.
- Classification software development: continue to improve for mass spectra; develop a similar shell for optical properties.

In summary:

1. Developed the technology to operate the particle mass spectrometer in the IR-UV operation mode. SPLAT-MS used to determine conditions for microorganism characterization using IR-UV evaporation/ ionization.

2. Bacterial culture samples with various cell densities were prepared and diluted to generate aerosols containing varying numbers of bacteria per milliliter.

3. Designed a single particle shape characterization system. The design of the optical system to accomplish this task is completed.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$105,000 |

Developing a New, Unified Systems Theory on Size Distributions of Atmospheric Particles

Yangang Liu

03-026

PURPOSE:

This project has a theoretical and a practical goal. The theoretical goal is to explore a paradigm-shifting theoretical framework on size distributions of aerosols, cloud droplets and raindrops that is entirely different from the mainstream theory. The practical goal is to apply the theoretical work to improve cloud parameterizations in climate models. The results derived from this work will also find additional applications in virtually all related areas, including comparison and integration of measurements from different instruments with various sampling scales, validation of satellite measurements by use of in situ aircraft measurements and coupling of numerical models of different scales. The success of the work will give BNL an edge in competing funding for ongoing and in future programs such as Atmospheric Radiation Measurement (ARM), Tropospheric Aerosol Program (TAP) and Water Cycle Program.

APPROACH:

Plan to empirically examine the issue of the size distribution universality and to seek applications of the systems theory to cloud parameterizations. Analysis of observational data and theoretical studies were carried out to achieve these objectives. Approaches for identifying size distribution universalities were first developed based on theoretical analysis. Data from aerosols, clouds and precipitation were then examined to investigate the size distribution

universalities using these approaches. A new analytical expression for the parameterization of the autoconversion process was theoretically derived by coupling the systems theory with a Kessler-type scheme. The details on the approaches are referred to the next section.

TECHNICAL PROGRESS AND RESULTS:

Progress was made on two fronts. First, two kinds of size distribution universalities were defined and examined using measurements. Size distributions belong to the universality of the first kind (hereafter first universality) if they statistically have a common normalized size distribution $f(x)$ given by

$$f(x) = \frac{D_s^n(D)}{N}, \quad (1)$$

$$x = \frac{D}{D_s}, \quad (2)$$

where D is the particle diameter; D_s and N are the mean diameter and total concentration of particles in the distribution. Figure 1 shows results calculated from some measurements, indicating that particle size distributions generally do not exhibit the first universality.

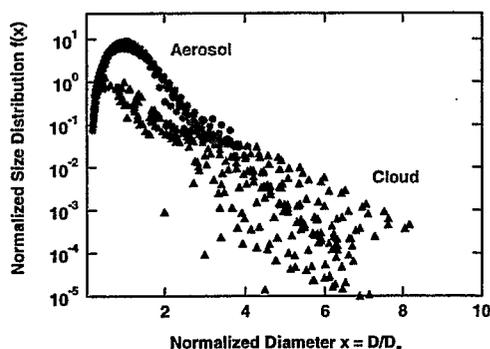


Figure 1. Illustration of the first universality of particle size distributions.

Size distributions belong to the universality of the second kind (hereafter second universality) if they statistically follow a common distribution family. To investigate the second universality, we examined the

relationship between a pair of dimensionless parameters: relative dispersion ε (defined as the ratio of the mean radius and the standard deviation of the size distribution) and the effective radius ratio β_e (defined as the ratio of the effective radius to the volume-mean radius). On the (ε, β_e) diagram, each point represents a size distribution. There is a unique relation between the two parameters for commonly used size distributions (e.g., lognormal, gamma, and Weibull). A collapse of the data points onto a specific $\beta_e(\varepsilon)$ curve suggests the second universality. Figure 2 shows the same data presented in Figure 1 in the (ε, β_e) diagram. It is clear that although particle size distributions generally do not exhibit the first universality, they do tend to assume the second universality. Furthermore, the results show that size distributions are well described by the Weibull distribution; this is consistent with the prediction by the systems theory.

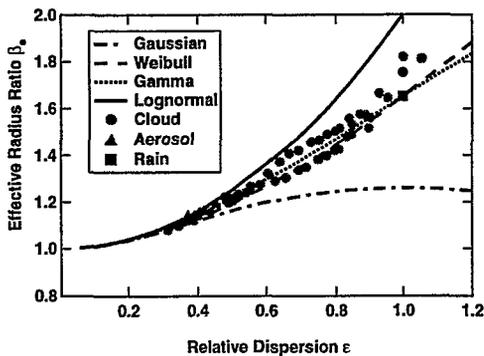


Figure 2. Illustration of the second universality of particle size distributions.

The other focus was on seeking applications of the systems theory to improve cloud parameterizations in climate models. A new parameterization for the autoconversion rate was theoretically derived by coupling the systems theory on rain formation with a Kessler-type parameterization that was recently developed at BNL. The new parameterization is given by

$$P = \left(\frac{3}{4\pi\rho}\right)^2 \kappa \left[\frac{(1+3\varepsilon^2)(1+4\varepsilon^2)(1+5\varepsilon^2)}{(1+\varepsilon^2)(1+2\varepsilon^2)} \right] N^{-1} L^3 H(r_6 - Rr), \quad (3)$$

$$r_c = 5.6084 \times 10^{-2} \left\{ \left[\exp\left(\frac{3 \times 10^{-17} N}{L}\right) - 1 \right] \frac{1}{L} \right\}^{1/6} = 0.99 \left(\frac{N}{L^2}\right)^{1/6}, \quad (4)$$

where P is the autoconversion rate from cloud water to rain water, ρ water density, κ a constant, ε the relative dispersion, N droplet concentration, L the liquid water content, r_6 the mean radius of the sixth moment and r_c the critical radius. The new scheme has three distinctive features compared to existing ones. First, it is theoretically derived instead of being empirically obtained and therefore each term has clear physical meaning. Second, unlike the existing schemes, it has no empirical parameters that have to be arbitrarily tuned. Third, it explicitly accounts for the effect of the relative dispersion on the autoconversion rate. The inclusion of the relative dispersion enables us to quantify the influence of aerosol-enhanced dispersion on the evaluation of the second indirect aerosol effect, the largest uncertainty identified in modeling climate change. Comparing the mean radius of the sixth moment against the critical radius as given by Eqs. (3) and (4) also provides a new way to simultaneously investigate the first and second indirect aerosol effects. As shown in Figure 3, the upward arrow along the line is the direction of increasing anthropogenic aerosol effect, i.e., aerosols increase critical radius but decrease the mean radius. Furthermore, when the mean radius of the sixth moment is larger than the critical radius, it rains. Evidently, rain is more difficult in continental clouds than in their marine counterparts, and on average continental clouds do not rain whereas marine clouds do.

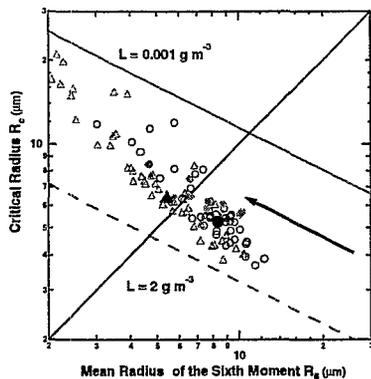


Figure 3. Relationship of the critical radius to the mean radius of the sixth moment. The open red triangles and black circles represent continental and marine clouds, respectively. The solid triangle and solid black dot are the average of all projects for continental and marine clouds. On the black diagonal line, the mean radius equals to the critical radius; below (above) this line there is (no) rain. The blue lines represent the relation between the critical radius and the mean radius of the sixth moment at limit liquid water contents $L = 0.001$ and 2 g m^{-3} .

These results have many important implications. For example, the existence of the second size distribution universality provides observational evidence for a unified theory on atmospheric particle systems that have been separately treated. The fact that size distributions tend to follow the Weibull distribution further lends support to the fundamental principals on which the current system theory is built. Use of the new autoconversion parameterization ends the common practice of arbitrarily tuning empirical parameters in climate models. The parameterization is

also applicable to models of smaller scales such as large eddy simulations and cloud-resolving models. Therefore, the parameterization has the potential to improve all cloud-related models, and puts us in a good position in funding competition.

It is now planned to analyze more data, examine fluctuation properties and scale-dependence, and to continue to advance the theory and seek further applications of the systems theory to the other key microphysical processes such as riming that need to be parameterized in climate models. There was close collaboration with P. Daum and R. McGraw on some of the issues that were addressed.

SPECIFIC ACCOMPLISHMENTS:

Publications:

Y. Liu, P. H. Daum, and R. McGraw, 2003: A new analytical expression for the critical radius in the autoconversion parameterization. *Geophys. Res. Lett.* (submitted).

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$45,000 |
| FY 2004 (budgeted) | \$45,637 |

Measurement of HO₂ Radicals by ChemiLuminescence Analysis of Atmospheric Radicals (CLAAR)

Stephen R. Springston

03-027

PURPOSE:

HO₂ radicals are a key intermediate in the generation of atmospheric smog. Quantitative measurements of HO₂ over a wide range of ambient conditions are essential for validation of the chemical models used to predict pollution events and design remediation strategies. We seek to develop a practical method for *in situ* monitoring that is suitable for wide-spread deployment. This effort complements continuing programs at BNL that address the effects of energy production on atmospheric processes.

APPROACH:

Computer modeling of chemistry in the atmosphere requires accurate representation of the relevant reactions and the initial conditions. The measurement community provides the data from which processes can be deduced and models are tested. The HO₂ radical is challenging to measure because of its low concentration and high reactivity. Existing analytical methods using laser-induced fluorescence are complex and not suited for broad deployment in monitoring networks.

Recently, Dr. Weinstein-Lloyd, SUNY Old Westbury, identified a chemical reaction used by biochemists for analysis of free radicals in cellular matrices. The reagent, a synthetic analogue of luciferin, is highly specific for the peroxy radical. We have collaborated with Dr. Weinstein-Lloyd to

apply this reaction to measure atmospheric HO₂ radicals by monitoring the resulting chemiluminescence with this reagent following collection into aqueous solution using instrumental techniques developed at BNL for atmospheric peroxides.

To calibrate the chemiluminescence output, we measure aqueous standards of analyte prepared by ⁶⁰Co γ -irradiation at the Chemistry Department of BNL. These standards are stable (< 1% decomposition) for 4-8 h. To further extend the method, we are developing a portable gas-phase transfer standard for field use.

Perfecting the chemical composition of the scrubbing solution, the aqueous standards and the reagent makeup has been carried out by Jun Zheng, a graduate student attending SUNY Stony Brook and working at BNL. The resulting instrumentation has the advantages of minimal weight, size and power consumption making it attractive for widespread deployment in monitoring networks and aboard aircraft platforms.

TECHNICAL PROGRESS AND RESULTS:

Instrumentation was assembled into a laboratory prototype to evaluate the technique. Methods to generate 'primary' aqueous standards, the reagent and scrubbing solutions were developed. As expected, the reagent stability, reaction sensitivity and signal background were all highly influenced by pH and buffer strength. After optimization of conditions, preliminary work showed a detection limit corresponding to an atmospheric concentration of ~0.7 pptv with a 2-min response time, more than suitable for expected ambient levels from 5 – 100 pptv. Interferences from naturally occurring levels of ozone and peroxides were shown to be

minimal. These results confirmed the 'proof of concept.'

Preliminary measurements of ambient air at BNL showed the expected correlation of HO₂ concentration with solar intensity. Short-term correlation with cloud cover was also observed. Complementary measurements of other species were needed in order to put these measurements of HO₂ in context. The laboratory instrument was thus deployed for twelve days during the summer of 2003 at Whiteface Mountain, NY. Data reduction has been completed and we are awaiting the complementary measurements of Particulate Measurements 2.5 and chemical speciation made at the site.

During the coming year, components will be assembled into a unit suitable for field deployment. This field unit will incorporate a temperature-stabilized reaction cell and electronics based on work with the laboratory prototype. A gas-phase transfer standard will be assembled which photolytically generates HO₂. This transfer standard will be referenced to the 'primary' aqueous standard. A gas-phase standard is necessary both to demonstrate the absence of inlet effects and to monitor instrument response during field operations.

Intercomparisons of this method with independent techniques at other institutions are being planned.

Commercial interests have requested information about our technique. We are exploring these possibilities through the BNL Office of Intellectual Property and Sponsored Research.

SPECIFIC ACCOMPLISHMENTS:

Zheng, J.; Springston, S. R.; Weinstein-Lloyd, J.; Quantitative Analysis of Hydroperoxyl Radical Using Flow Injection Analysis with Chemiluminescence Detection, *Anal. Chem.* 75, 4696-700, 2003.

Weinstein-Lloyd, J. B.; Zheng, J.; Springston, S. R.; Hydroperoxyl Radical Detection by MCLA Chemiluminescence, American Meteorological Society 84th Annual Meeting, Sixth Conference on Atmospheric Chemistry, Seattle, WA January 2004.

Zheng, J.; Weinstein-Lloyd, J. B.; Springston, S. R.; Development of a Chemiluminescence Method for Gas-Phase HO₂ Detection, *Eos Trans. AGU*, 84(46), Fall Meet. Suppl., Abstract A22G-05, San Francisco, CA, December 2003.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$100,000 |

Chemistry of the Rhizosphere

Mark Fuhrmann

03-030

PURPOSE:

Reactions take place around plant roots on the scale of mm to μm with elemental abundances in mmols; a region where the unique tools at the NSLS can be applied effectively. In this work, we explore processes that take place in the rhizosphere, by which the uptake and sequestration of contaminant metals (e.g. As and Zn) in living plants are controlled. The goal is to develop methods to examine living plants at the NSLS in which the speciation and distribution of metals around roots can be determined. Developing the techniques and building the expertise to interpret and disseminate the information that will be evolved, will establish a new area of expertise at BNL.

APPROACH:

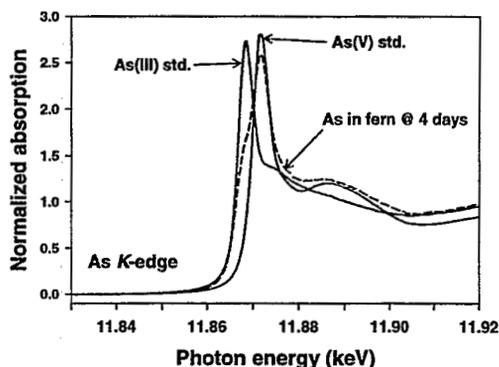
Some plant species can hyperaccumulate certain metals while other closely related species cannot. Our approach is to examine the behavior of metals at roots of a hyperaccumulator and a related non-accumulator to assess the mechanisms of metal sequestration and transport at roots of these important plants. We focus on two hyperaccumulators, *Thalpi caerulescens* which hyperaccumulates Zn and *Pteris cretica* which hyperaccumulates As. The As work is being conducted for a Masters Thesis by Marianna Kissell of SUNY Stony Brook.

Synthetic complexing agents are very useful for eluting contaminant metals from soil and a few also induce enhanced accumulation in the roots and shoots of plants. These reagents (primarily EDTA and DTPA) have

been shown to increase plant uptake of a variety of contaminants including Pb and ^{241}Am . However, it is not clear *how* these reagents act to enhance uptake and translocation to above-ground parts of the plants. Do the complexes break down at the roots? This is the question being addressed in collaboration with David Singer, a graduate student at Stanford U.

TECHNICAL PROGRESS AND RESULTS:

Arsenic in *P. cretica*. Hydroponic uptake of As (V) is rapid (As in plant shoots exceed 1000 ppm in hours) with no conversion to As (III) over a day or two and no ill effects on plant health. With the introduction of sodium arsenate solution to the soil, the uptake into the roots and translocation to above ground biomass is rapid and initial x-ray absorption near edge structure (XANES) spectra for arsenic in live leaves is consistent with an aqueous As(V) species. Other XANES spectra collected over time show that after four days As(V) in the leaves is being reduced to an As(III) species (Fig. 1).



Live leaf XANES data collected at 150 days suggest nearly all arsenic present is being maintained as aqueous As(III) in the living leaves. XANES analysis of dying leaves suggests rapid reoxidization to an As(V)

species. This has important implications for fate and transport of As in soils.

EDTA – Metal Complexes in Plants. In this work we have used infrared spectroscopy to identify a variety of metal-EDTA complexes and subsequently sought those complexes in plants exposed to them. The issue is: does the complex remain intact in the plant or is it degraded? We observed, using an attenuated total reflectance cell, unique differences in the spectra for the various metals tested. The work under the LDRD was to search for that signal in plants. This is difficult because of water and competition by natural plant materials having absorption bands throughout the spectral region. We believe that we do see a very weak signal in FT-IR maps of plant roots and stems that have been exposed to Pb-EDTA solutions. This signal does not appear in controls. Further analysis of these data is in progress.

Zn hyperaccumulators. We determined Zn distributions around plant roots, and its' speciation in the hyperaccumulating plant, and its related non-accumulator. Initially we used agar (spiked with nutrients and Zn) to act as a substrate for plant growth. We found that the best approach is to grow the plants in a sandy soil, remove them carefully and place the rinsed roots onto the substrate. This allows a discrete time period of exposure. Synchrotron microbeam x-ray fluorescence was able to distinguish the roots from the agar, and we observed what we believe to be Zn distributions around the roots that may be the result of the diurnal cycle of the root drawing Zn in solution toward the root and then a nighttime release of exudates that moved the Zn away. For this experiment the agar was frozen and this

gave serious problems in seeing and photographing the root. Attempts to use unfrozen samples resulted in serious x-ray beam damage to the sample. Now a method has been developed that allows x-ray analysis without beam damage and that also allows the plants to be exposed to low solubility compounds. We used silica flour mixed with the reagent, added water to make a paste, and then pressed the mixture into a cell. The plant roots can then be spread out on this layer and a mylar window added. This method presents a much more realistic approach to the chemistry and physics of the root in soil compared to our initial hydroponic experiment. Data from a recent run are now being reduced to determine if there are differences in Zn speciation among the hyperaccumulator and the non-accumulator plant, as a function of Zn compound added to the substrate.

SPECIFIC ACCOMPLISHMENTS:

M. Kissell, R. Reeder, and M. Fuhrmann, Uptake of arsenic by *Pteris caudata*: in-situ XANES study of living plants, NSLS Annual Users' Meeting, 2003, Poster Presentation.

M. Kissell, R. Reeder, and M. Fuhrmann, In-situ XANES study of arsenic uptake in a living fern, American Chemical Society Annual Meeting Sept., NYC, Oral Presentation.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$102,157 |

Integrated Analysis of Carbon and Nitrogen Metabolism in Plants and Subsequent Analysis of Photosynthetic Acclimation to Growth in Elevated $p\text{CO}_2$

Alistair Rogers

03-039

PURPOSE:

The objective of this project is to develop new capabilities at BNL for plant physiological analysis with an emphasis on the response of carbon and nitrogen metabolism to environmental change.

The expected result of this project is to increase the analytical capabilities at BNL and to establish it as a leading laboratory for the analysis of carbon and nitrogen metabolism in plants responding to global change. This project supports BNL's strategic initiative to increase investment in carbon cycle science and the scientific goals of the *Climate Change Research Division* of BER.

APPROACH:

A sustained and maximal stimulation of photosynthesis and growth in future partial pressures of carbon dioxide ($p\text{CO}_2$) is dependent on an adequate supply of nutrients, principally nitrogen, and the ability for carbon sinks to utilize the additional photosynthate produced at elevated $p\text{CO}_2$. Currently, there is a gap in the scientific understanding of how carbon and nitrogen metabolism interact at elevated $p\text{CO}_2$ and how this interaction determines plant responses to global change. Furthermore, within the global change biology community there is a gap in the technical expertise necessary to undertake a

detailed mechanistic evaluation of carbon and nitrogen metabolism.

This project aims to fill the gap in both the technical capabilities for, and scientific understanding of, the interaction of carbon and nitrogen metabolism at elevated $p\text{CO}_2$. In order to fill the technical gap, it is necessary to gain additional skills in the analysis of nitrogen metabolites to augment a suite of analytical techniques applicable to the scientific problem. Improved scientific understanding of the interaction between carbon and nitrogen metabolism in elevated $p\text{CO}_2$ will be achieved through collaboration with Dr. Stephen Long and Dr. David Karnosky by undertaking detailed studies of soybean and aspen grown in the field using Free-Air CO_2 Enrichment facilities at the University of Illinois at Urbana Champaign (SoyFACE) and the Harshaw Experimental Forest, Rhinelander, WI (Aspen FACE).

TECHNICAL PROGRESS AND RESULTS:

In the winter of 2003 Alistair Rogers undertook a period of training at the Max Planck Institute for Molecular Plant Physiology, Golm, Germany, in the laboratory of Dr. Mark Stitt and acquired the skills necessary to analyze nitrogen metabolites. Throughout FY 2003 analysis of material collected prior to this LDRD has been completed, and a second season of material has been collected and analysis is underway. It is anticipated that in FY 2004 the biochemical analysis of soybeans will be completed.

Analysis of soybeans grown at elevated $p\text{CO}_2$ at the SoyFACE experiment demonstrated that even in field conditions plants grown at elevated $p\text{CO}_2$ had a reduced leaf nitrogen content (Figure 1). However, the reduction in leaf N content was confined to the start of the season. By the middle of the growing season, an increased supply of

amino acids for protein biosynthesis was observed in plants growing at elevated $p\text{CO}_2$ (Figure 2). It is hypothesized that plants grown at elevated $p\text{CO}_2$ were better able to utilize an increased supply of ureides from *Rhizobia* (data not shown) because the excess photosynthate produced at elevated $p\text{CO}_2$ provided the carbon skeletons necessary for amino acid biosynthesis (Figure 3).

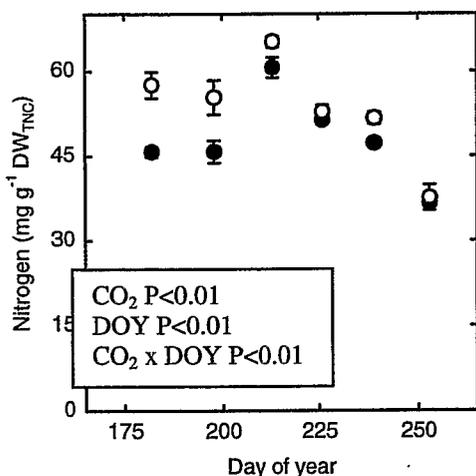


Figure 1. Leaf nitrogen content measured at six time points in soybeans grown throughout their life-cycle at elevated (55Pa) $p\text{CO}_2$ (filled circles) and current (37Pa) $p\text{CO}_2$ (open circles) in the field using Free Air CO_2 Enrichment technology. Data are mean \pm SE, $n=4$ replicate FACE rings.

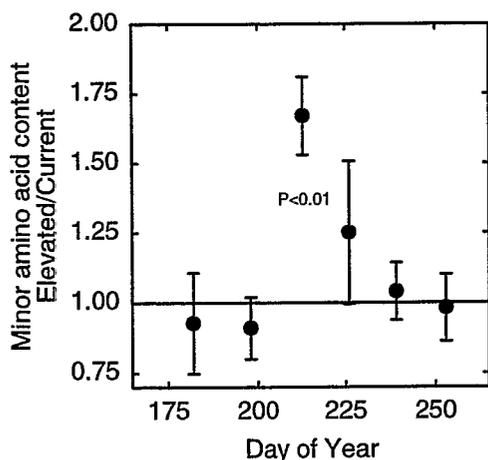


Figure 2. The ratio of the content of minor amino acids at elevated $p\text{CO}_2$ to that at current $p\text{CO}_2$ for the soybeans described in Figure 1.

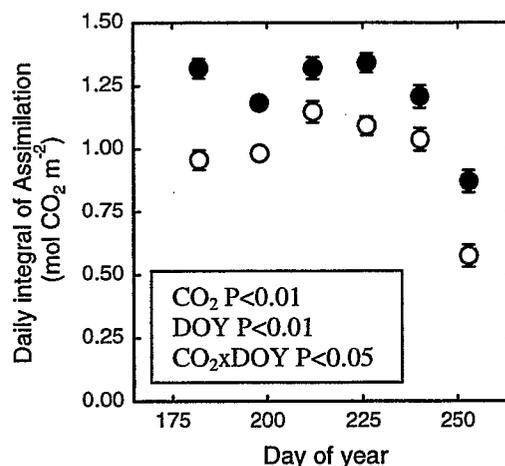


Figure 3. The daily integral of net CO_2 assimilation for the soybeans described in figure 1

SPECIFIC ACCOMPLISHMENTS:

Presentations

Poster: *American Society of Plant Biologist, Honolulu, HI.* Rogers, A.; Gibon, Y.; Wittig, V.; Bernacchi, C.; Stitt, M.; Long, S.P. Dynamics of carbon & nitrogen metabolism in field-grown soybean grown throughout its life cycle in elevated carbon dioxide.

Poster: *DOE Terrestrial Carbon Processes Meeting, Boulder, CO.* Rogers, A.; Gibon, Y.; Wittig, V.; Bernacchi, C.; Stitt, M.; Long, S.P. Dynamics of carbon & nitrogen metabolism in field-grown soybean grown throughout its life cycle in elevated carbon dioxide.

Talk: *Annual Meeting American Society of Agronomy, Crop Science Society of America & Soil Science Society of America, Denver, CO.* Rogers, A.; Gibon, Y.; Wittig, V.; Bernacchi, C.; Stitt, M.; Long, S.P. Carbon & nitrogen dynamics of soybean grown in the field under elevated levels of carbon dioxide.

Talk: *Ecological Society of America, Tucson, AZ* Leakey ADB, Davey, P.; Rogers, A.; DeLucia, E.; Drake, B.; Murthy, R.; Karnosky, D.; Long, S.P. How will leaf respiration in the dark respond to elevated [CO₂].

Publications

Rogers, A.; Gibon, Y.; Wittig, V.; Bernacchi, C.; Stitt, M.; Long, S.P. Dynamics of carbon & nitrogen metabolism in field-grown soybean grown throughout its life cycle in elevated carbon dioxide. (in preparation)

Leakey ADB, Davey, P.; Rogers, A.; DeLucia, E.; Drake, B.; Murthy, R.;

Karnosky, D.; Long, S.P. (2003) How will leaf respiration in the dark respond to elevated [CO₂]. (in preparation)

Funding Received

DOE, \$100,000 for capital equipment request made based on skills acquired as a result of this LDRD. Equipment purchased will allow all the skills acquired in the analysis of nitrogen metabolites to be transferred to BNL.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$66,000 |
| FY 2004 (budgeted) | \$67,924 |

Evaluation of High-Energy Radiation Effects in Materials

Charles C. Finfrock
G. A. Greene

03-050

PURPOSE:

Propose to design, construct and demonstrate a portable, compact and versatile radiation-effects vacuum cryostat to provide a capability to measure a wide spectrum of radiation effects in materials. Small-scale facilities at which to measure radiation effects in proton and heavy ion beams at BNL are no longer functional. However, the need to quantify such effects is immediate and increasing as the applications for high-energy high-intensity protons, as well as, high-energy heavy ions increases.

Some of the radiation effects to be investigated include radiation damage in metals, radiation damage in high temperature superconductors, energy deposition, and efficiency of low-Z shielding against heavy ions for deep-space exploration.

APPROACH:

In recent times, applications of radiation effects to particle accelerators have risen in prominence with the introduction of facilities such as the AGS-RHIC-NSRL at BNL (Alternating Gradient Synchrotron-Relativistic Heavy Ion Collider-NASA Space Radiation Laboratory) and in addition facilities at Los Alamos National Laboratory and Oak Ridge National Laboratory to name a few. Projects on the drawing board such as Muon Collider, and the Rare Isotope Accelerator promise to motivate investigators to pursue additional studies into materials behavior and radiation effects previously overlooked, such as shielding

against galactic heavy ions and transmutation of novel reactor fuels. Computational models for radiation effects could benefit from the availability of experimental data against which the models could be validated.

We have explored a variety of radiation effects in recent years, such as proton damage to superconductors, cryogenic energy deposition in magnet materials, and measurements of defect production in metals by the measurement of resistance changes, all of which were small-scale experiments that could have benefited from the availability of a general-purpose, small-scale radiation effects test facility.

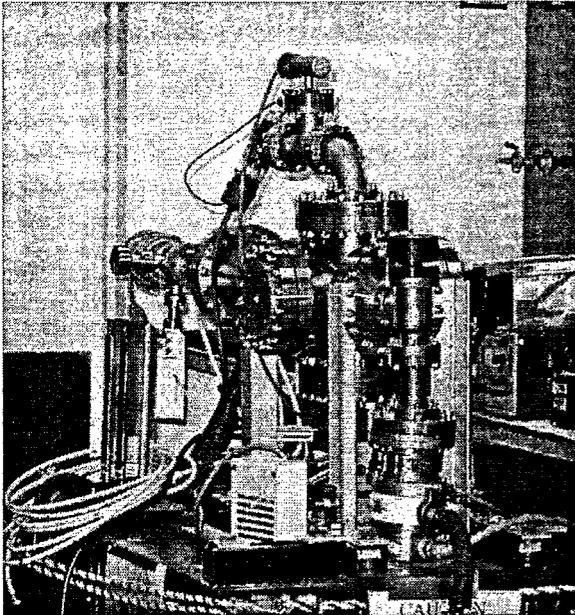
TECHNICAL PROGRESS AND RESULTS:

The vacuum-cryostat apparatus has been constructed with Conflat components and successfully tested to 3 K and 5×10^{-9} Torr. A general-purpose data acquisition system has been assembled of Keithley components that operates on a computer-controlled platform called Test Point. General-purpose data acquisition and control software has been developed that provides an interactive interface with the experimental hardware.

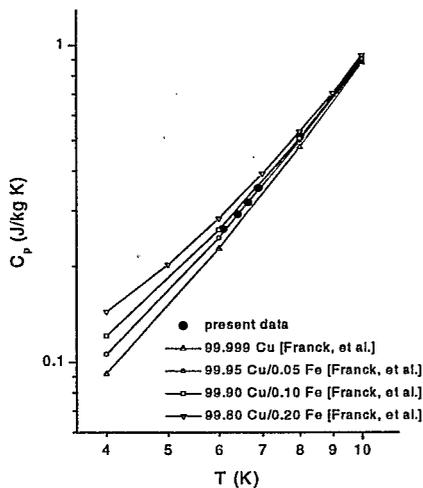
Accurate and high-precision measurements of voltage, current, and resistance have been made of a variety of test objects and transducers through a 250-ft long twisted-shielded multiconductor instrumentation cable for beam line operations. Cryogenic temperature measurements, as well as, measurements of the temperature-dependent resistance of thin-wire radiation damage, targets of copper and tungsten have been made to verify the accuracy and precision of the measurement system at liquid helium temperatures. A series of energy deposition measurements were performed on a copper calorimeter to measure the specific heat of

the calorimeter target below 10 K, and the Kondo effect on the resistance of the radiation-damage wire targets was measured down to 3 K as further verification of the performance of the integrated system.

The assembled and operational radiation-effects apparatus is shown below.



The measured specific heat data for the copper calorimeter target are shown below.



SPECIFIC ACCOMPLISHMENTS:

Publications:

Greene, G. A. and Finfrock, C. C.; "Measurements of the Specific Heat of High-Purity Copper at Temperatures Below 8 K by a Modified Pulse-Heating Technique," Int. J. Experimental Thermal and Fluid Science, 27(1), pp. 111-119 (2003).

Greene, G. A.; Finfrock, C. C.; Snead, Jr., C. L.; Hanson, A. L.; and Murray, M. M.; "Energy Deposition in a Thin Copper Target Downstream and Off-Axis of a Proton-Radiography Target," Nucl. Instr. and Meth. B, 197(3/4), pp. 247-258 (2003).

Future Funding Prospects:

NASA - Office of Biological and Physical Research, Physical Sciences Research (three proposals submitted to NASA for FY 04 funding to use this facility at NSRL for shielding evaluation).

DOE-Nuclear Energy, AFCI Program (two proposals submitted to LANL in fuels development and transmutation science for possible FY 03 funding to use methods being developed under this LDRD).

DOE-Office of Science, Rare Isotope Accelerator Program (discussions underway for FY 04 funding to apply this capability to measure proton-induced radiation damage in high temperature superconductors).

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$106,000 |

Structural Properties of Methane Hydrates

Devinder Mahajan

03-056

PURPOSE:

Modify and utilize the existing methane hydrate unit at BNL to collect and model reproducible decomposition data under subsurface conditions that will aid in understanding the kinetic stability of methane hydrate. Measure and correlate physical properties of field samples of host sediments from methane hydrate sites.

APPROACH:

The global abundance of methane hydrate makes it a promising future energy source. The key to recovering high (~15 wt%) CH₄ content of methane hydrate is to determine precise conditions of its kinetic stability in host sediments. An uncertainty remains as to the nature of sediment pores in which methane hydrates prefer to form and reside. Our approach involves: 1) measuring temperature and pressure dependent decomposition kinetics in a modified BNL methane hydrate unit and 2) imaging field samples of sediments from the methane hydrate sites using Computed Microtomography (CMT) to measure porosity and other properties.

Collaborations have been established with 1) Dr. W. Winters of the United States Geological Survey (USGS), Woods Hole, to obtain pristine samples of host sediments and to utilize their GHASTLI apparatus (Gas Hydrate and Sediment Test Laboratory Instrument) to measure complementary methane hydrate properties and 2) Dr. K. Jones to measure porosity and related properties of the host sediments at Beamline

X27A at the NSLS (National Synchrotron Light Source).

TECHNICAL PROGRESS AND RESULTS:

A unit, previously used for gas and oil research, has been modified to conduct methane hydrate studies. The unit was recently commissioned to study decomposition kinetics. In parallel, a series of host sediment samples from Blake Ridge, a well-established methane hydrate site off the coast of the Carolinas, were obtained through USGS. Of these, three samples were selected to establish their porosity differential as a function of depth at 0.2 m, 50 m, and 667 m. The CMT technique was used to collect 2-D data on the sediment slices, from which 3-D images of the sediments were reconstructed. Further data refinement now continues.

In FY 2004, a cell capable of operating at high pressures and low temperatures (those mimicking ocean floor conditions) is being constructed to study *in situ* methane hydrate formation in host sediments. This data will be crucial to establish the specific sites that allow facile methane trapping to form clathrate hydrates. A complementary decomposition data collection in the hydrate unit will allow us to develop a kinetic model.

SPECIFIC ACCOMPLISHMENTS:

Refereed Publications

1. Kinetic Reproducibility of Methane Production from Methane Hydrates. P. Servio and D. Mahajan. Topics In Catalysis, in preparation.
2. Methane Hydrate Studies: Decomposition Kinetics and Delineating Properties of Host Sediments. D. Mahajan, P. Servio, K.

W. Jones, H. Feng, and W. J. Winters. Book Chapter in Advances In Gas Hydrates, in preparation.

3. Characterization of Methane Hydrate Host Sediments Using Synchrotron Computed Microtomography. D. Mahajan, K. W. Jones, H. Feng, W. J. Winters, and P. Servio. American Mineralogist, submitted (2003).

Presentations

- Gulf of Mexico Naturally Occurring Gas Hydrates JIP Workshops. Denver, CO. D. Mahajan. September 30 - October 1, 2003.
- Kinetic Reproducibility of Methane Production from Methane Hydrates. P. Servio and D. Mahajan. Symposium on Synthetic Clean Fuels from Natural Gas and Coal-bed Methane: 30 Years Since First Oil Crisis. Co-sponsored by the ACS (American Chemical Society) Fuel and Petroleum Chemistry Divisions.

226th ACS National Meeting, New York, NY. September 7-11, 2003.

- Methane Hydrate Studies: Delineating Properties of Sediments Using Synchrotron Computed Microtomography (CMT). D. Mahajan, K. W. Jones, H. Feng, and W. J. Winters. Presented at the Symposium on Gas Hydrates, 2003 AICHE (American Institute of Chemical Engineers) Spring National Meeting, Abstract #78a, New Orleans, LA. March 30 - April 3, 2003.

Review Presentation

- Methane Hydrate Activity at BNL - An Overview. D. Mahajan. To NETL/DOE. May 5, 2003

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$ 85,000 |
| FY 2004 (budgeted) | \$104,000 |

Dynamics of Wind Turbine-Tower-Foundation Systems

Aristodimos J. Philippacopoulos 03-061
M. L. Berndt

PURPOSE:

Within the framework of initiating a BNL research program in wind energy, this project investigates aspects of structural dynamics and materials engineering for both on-land and offshore wind installations. We are focusing on: (a) dynamic analysis of combined wind turbine-tower-foundation systems and (b) response behavior of foundation materials. Methods and material data expected from this program will help BNL to establish a position within the wind energy community.

APPROACH:

This program has two components: (a) structural dynamics and (b) materials engineering of turbine-tower-foundation systems.

(a) Structural Dynamics: Understanding the dynamic response of the complete wind turbine-tower-foundation system, as a whole, is fundamentally needed in order to make decisions about improving their performance and reliability. The underlying motivation is that efficiency, reliability, and cost reduction studies require good knowledge of how close we can predict the dynamic response of wind turbine systems.

We are developing a substructure approach for the dynamic response analysis of wind turbine systems. It breaks down the total systems into three key components: turbine, tower and foundation. The motion of each of them is mathematically treated separately. Then by invoking interface conditions, the

dynamics of the whole system is obtained. We believe that such an approach is innovative in that it allows each component to behave dynamically as is without imposing *a priori* constraints. This implies accurate modeling and better correlations with measured wind turbine responses.

A computer implementation of our approach is concurrently being pursued under this LDRD. For this purpose the Compaq Visual Fortran is used. Pavan Vaddadi, a Ph.D student from Stony Brook University, is collaborating with the computer implementation task.

(b) Materials Engineering: Concrete foundations represent a significant proportion of wind farm construction costs. In addition, production of cement used in concrete is very energy- and CO₂-intensive. In this LDRD, we investigate the potential use of sustainable and fibre reinforced concrete for wind turbine foundations. Sustainable concrete includes the use of recycled and waste materials as partial replacement for cement, in order to reduce the environmental and energy impact of the concrete, as well as the cost. Fly ash and blast furnace slag are used for this purpose. Different concrete mix designs are being evaluated for mechanical properties, thermal properties and durability. In addition, the potential use of recycled concrete as an aggregate is being investigated in collaboration with Mariola Sullivan (Plant Engineering/Stony Brook University).

TECHNICAL PROGRESS AND RESULTS:

This project was started by focusing on mathematical modeling of wind turbine systems on the basis of elastodynamic theory. In this regard, the system was treated in the 3D space. The total motion was composed of rigid body and elastic

components. A detailed development of the equations of motion of wind-turbine-tower-foundation systems was undertaken and completed. This advances the state-of-the-art in this area as it offers a complete coupling, thus allowing all significant dynamic interactions to participate in composing the wind response of the system. Following this development, the project investigated solution techniques to tackle the equations of motion. We are now following frequency domain analysis using a variety of transfer functions. The latter were obtained from our mathematical modeling, and selected to represent system responses that are essential in evaluating system performance. In FY 04 we are continuing with the code development. Our aim is to have a working version of the code by the end of FY 04 that can be used in subsequent research. For example, automation, graphics and pre and post processing capabilities will be kept to a minimum. Instead, our work will focus on benchmarking and verification tasks, which will offer credibility to the code.

With regard to the materials investigation, a series of three sustainable concrete mixes and one control mix has been designed and testing of these has commenced. Compressive strength versus time tests has been completed. These tests have indicated the rate of strength development for different sustainable concrete mixes. It was determined that mixes with 50% blast furnace slag had the best performance in this respect, whereas mixes with 50% fly ash did not meet the desired strength requirement of 40 MPa.

Initial permeability tests on sustainable concrete formulations have been completed. The results show that slag-modified concrete had permeability of the order of 10^{-10} cm/s and this is within the desired range for durable concrete. In contrast, the

permeability for concrete with a high volume of fly ash was of the order of 10^{-9} cm/s. Blending both slag and fly ash led to a decrease in permeability.

Fibre reinforced sustainable concrete mixes have been cast and are currently undergoing long-term durability tests. The first of the durability assessments is exposure to artificial seawater. Tidal action is being simulated in order to evaluate the performance of the concrete in offshore applications. Potential corrosion of the embedded steel fibre is being studied, along with any degradation of the concrete. To date, the tests indicate that only fibres close to the exposed surface are susceptible to corrosion. Other durability tests are in progress to determine the resistance of the concrete mixes to sulphate attack and carbonation in aggressive groundwater for onshore applications.

Characterization of the sustainable and fibre reinforced concrete mixes will continue in FY 04. The durability tests will be completed and these will give a comparative evaluation of the performance of the materials in seawater and deleterious groundwater conditions. Other tests to be completed in FY 04 include determination of elastic and thermal properties for use in the modeling component. Damping characteristics and pullout strength may also be investigated.

SPECIFIC ACCOMPLISHMENTS:

Presentation and abstract for American Wind Energy Association Windpower 2003 Conference, Austin, TX. May 2003.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$140,000 |
| FY 2004 (budgeted) | \$146,000 |

Investigation of Neutron and Gamma Probes to Detect Explosives in Sealed Containers

Michael Todosow
L. Wielopolski

03-064

PURPOSE:

The purpose of the project is to examine options for using neutrons and/or resonance gamma rays to probe airline-shipping containers and determine the presence of explosives by reading the characteristic signatures of induced or scattered radiation. These techniques can be specifically designed to probe for contraband in small and large containers. The challenges include the ability to make them simultaneously effective and efficient. This includes issues such as decreasing false positive alarms while retaining a very high detection probability, reducing the time necessary to make the determinations, cost and implementation issues, etc.

APPROACH:

It is proposed to use modern Monte Carlo methods (specifically the MCNP/MCNPX codes developed by LANL (Los Alamos National Lab)) to perform "synthetic experiments" to simulate systems based on the use of neutrons and resonance gamma rays to determine the physical and performance characteristics of potential systems to achieve these missions. However, because neutrons will activate materials, the focus will be on Gamma Resonance Technology (GRT), which has been demonstrated to be a viable solution to intercept concealed explosives with a low (5%) false alarm rate. A fundamental aspect of the initial phase of the study will be to

evaluate the adequacy of the basic cross section data needed to evaluate this approach (e.g., the photon cross section for nitrogen). This has multiple ramifications.

Based on the results of the initial survey phase, additional analyses will be performed to define and optimize a reference system(s), which might be based on neutrons only, resonance gamma only, or a combination. Initial experiments will then be planned to evaluate selected performance characteristics, e.g., intensity, number and orientation of neutron/gamma sources; number and orientation of detectors; characteristics of signatures to be measured/compared, etc.

TECHNICAL PROGRESS AND RESULTS:

The list of accomplishments for FY 03 includes:

Nuclear Data (P. Oblozinsky and A. Aronson).

Data for the 9.17225 MeV gamma resonance in N-14 was provided by the NNDC (National Nuclear Data Center), processed via NJOY and incorporated into the MCNP (Monte Carlo N-Particle) library. NNDC has also developed the gamma resonance data for O-16. Approaches for incorporating the data for additional isotopes into the MCNP libraries in a more systematic way are being explored.

Monte Carlo Simulations (I. Dioszegi, A. Hanson, M. Todosow, and L. Wielopolski).

MCNP models of the source- (container + explosive) detector geometry were developed and simulations performed examining the detector response on- and off-resonance to evaluate detectability. The

“reference” configuration contains a nitrogen-bearing explosive, in an LD3 airline container filled with other nitrogen-bearing material. The effect of several variations from “reference” conditions was evaluated, including:

- The effect of an energy distribution for the source vs. mono-energetic beams.
- Varying the size/quantity and shape of the explosive.
- Initial studies comparing transmission and reflection/fluorescence were initiated.
- An initial estimate was made for the time required to achieve a desired detection confidence level based on a simplified analytic approach, and a “clustering technique” to minimize the scanning time required.

In FY 04 the plan is to address the following issues:

- Consider the engineering and nuclear issues involved in the design of a C¹³ target. Ideally, this will require data for the production of gamma rays via the interaction of protons with the target.
- Other materials are potential options for use with the GRT approach (e.g., O¹⁶, Cl³⁵, C¹², Ca⁴⁰). The resonance gamma data for these materials must be acquired and implemented into the MCNP modeling framework.
- The bulk of the analyses performed in FY 03 considered detection by examining the change in the transmitted probing gamma ray as it passed through a container. The ability to detect explosives by having both the source and the detection on the same side of the object offers potential operational advantages and various configurations will be examined.

SPECIFIC ACCOMPLISHMENTS:

Presentations

Application of Monte Carlo Code for a Gamma Resonance System Analysis, Wielopolski, L.; Hanson, A.; Dioszegi, I.; Todosow, M., **Poster presented at Gordon Research Conferences, Conference on Illicit Substance Detection: Explosives**, Il Ciocco, Barga, Italy, June 8-13, 2003.

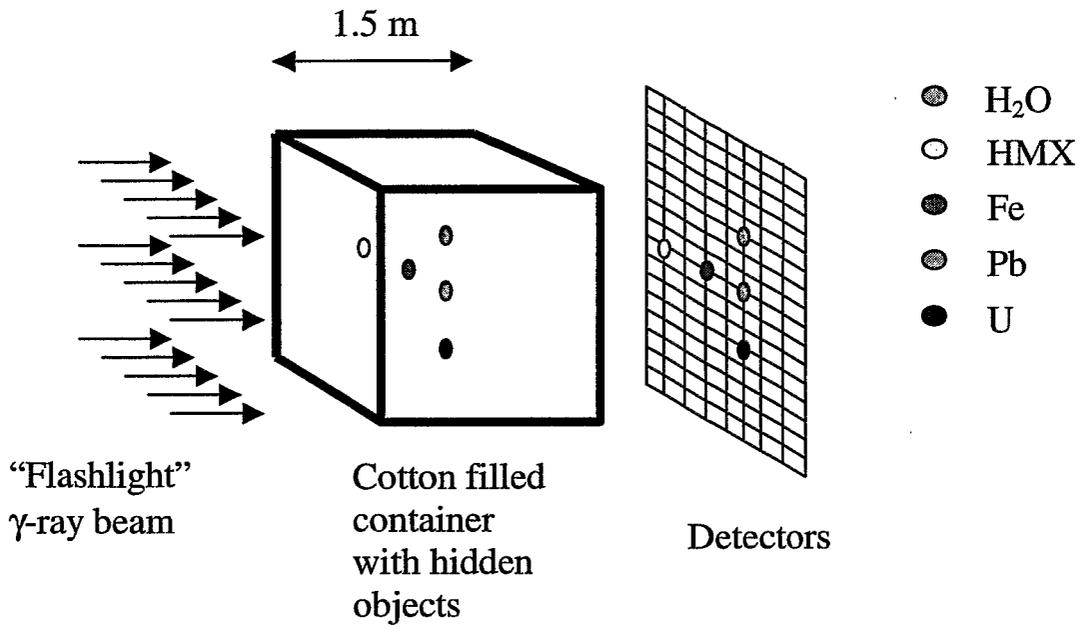
Proposals

- BAA NUMBER: DAAD05-03-T-0024: Efficient Detection of High-Z materials in Cargo.
- Radiological/Nuclear Countermeasures Program Proposal, Multi-Scanning System for Large Cargo Containers Inspection for SNM (special nuclear material) and Explosives Detection (submitted to the DHS (Department of Homeland Security)).

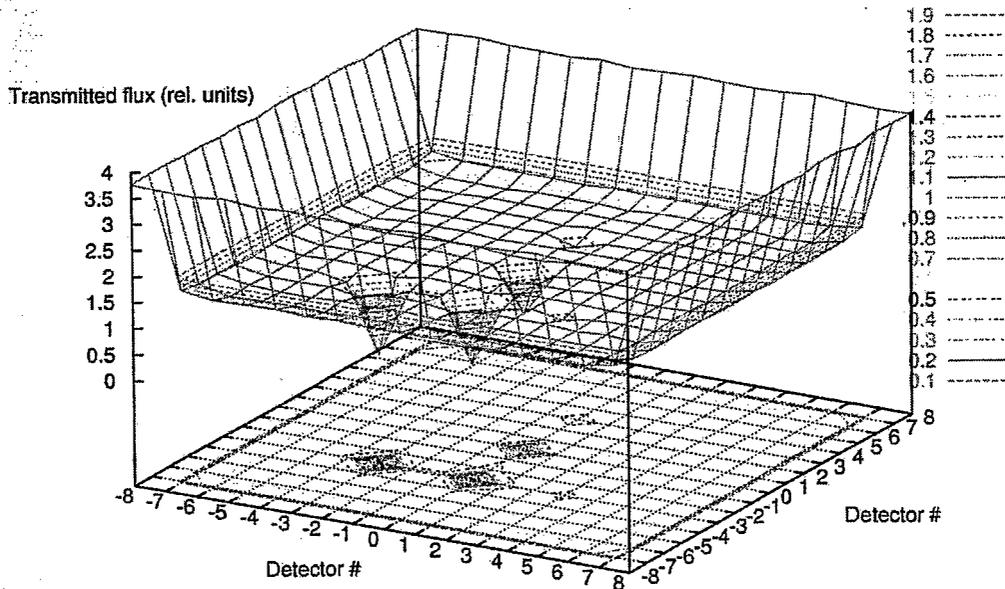
LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$110,000 |
| FY 2004 (budgeted) | \$115,000 |

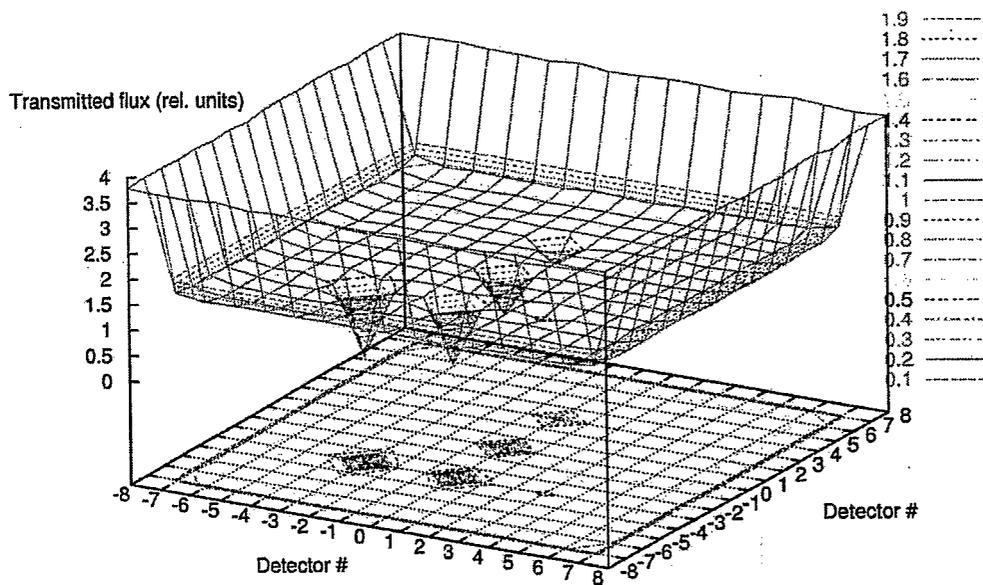
**Results from MCNP Simulations of Explosives in LD3 Airline Container
Off-Resonance, On-Resonance, and Difference**



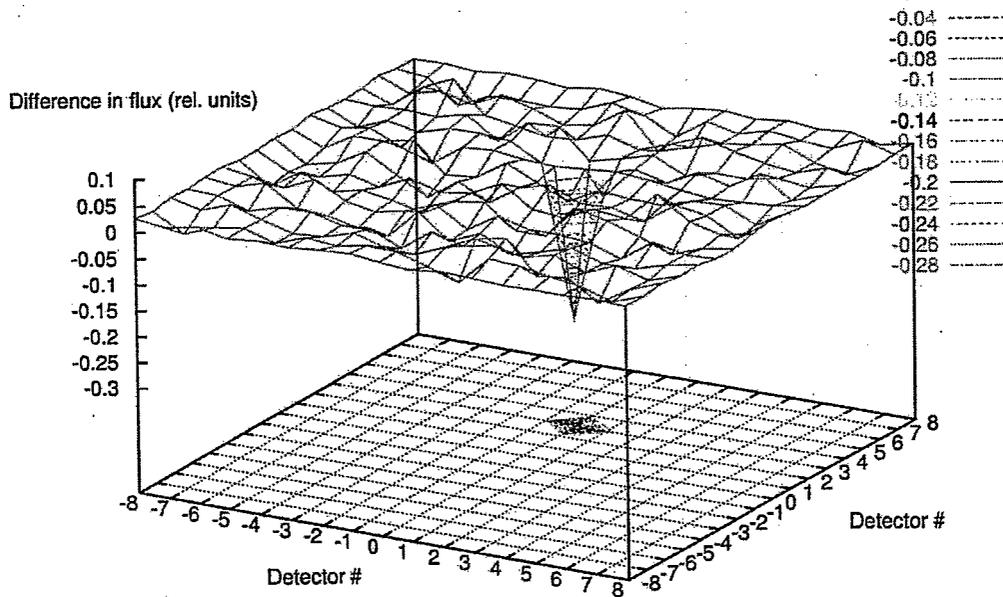
9 MeV gamma-ray shadow image of r=27 mm objects (H₂O, HMX, Fe, Pb, U)



9.17 MeV (100 eV dist.) gamma-ray shadow image of r=27 mm objects (H₂O, HMX, Fe, Pb, U)



9.17 MeV (100 eV dist.) on resonance - 9 MeV off resonance image of r=27 mm objects (H₂O, HMX, Fe, Pb, U)



Ultrasound and Infrared Imaging to Detect Degradation of Electric Cable Insulation

Michael Villaran

03-065

R. Lofaro

PURPOSE:

The objective of this research is to evaluate the use of ultrasonic stimulation coupled with infrared imaging as a new non-destructive inspection method for monitoring the condition of electric cables. The technique, which has the potential for identifying and locating many types of electrical insulation damage that are not readily detectable using currently available condition monitoring methods, is fast, does not require disturbing the tested cable and is easily adaptable to in-plant inspection.

Successful development of this technique would be of great value to nuclear utilities and the Nuclear Regulatory Commission (NRC) who continue to fund research in cable testing methods to support license renewal and nuclear plant life extension initiatives. This work fits in with BNL's Nuclear Renaissance strategic initiative to involve the laboratory in developmental research for next-generation advanced reactor designs and their support technologies. The Federal Aviation Administration (FAA) and the National Aviation and Space Administration (NASA) have also committed extensive resources to the development of new techniques that can provide a more accurate assessment of wiring conditions in aircraft and space vehicles than are presently available.

APPROACH:

Beginning in 1994, BNL has served as the lead laboratory for the NRC Office of Research (RES) in a research program to study the effects of service aging on electric cables in nuclear power plants and techniques for evaluating the condition of cables. During this time, interest in inspection techniques developed that employed ultrasonic stimulation coupled with infrared imaging to identify hidden cracks, disbonds, and other defects in cast and forged metal parts, ceramics and certain types of polymers. The types of defects that the technique was effective at identifying resembled the defects and degradation in polymeric cable insulation that we have observed.

The initial thrust of the research concentrates on the proof-of-concept: to validate the use of ultrasound stimulation coupled with infrared detection as a viable condition monitoring technique for electrical insulation, an application in which it has never before been tried. Using typical nuclear plant cables, whose degradation characteristics are well understood from previous research, parametric studies of the test equipment variables will be conducted to optimize the ultrasonic stimulation of the cable insulation in order to maximize detection of defects through infrared imaging. To be most practical, the technique should be able to reliably detect defects at a reasonable distance from the point of application of the ultrasonic probe. By generating surface waves we will try to maximize the detection distance; application of the ultrasound directly into the copper conductor may also achieve increased detection distance. BNL has been interfacing with one of the technique's

developers, Dr. Austin Richards, of Indigo Systems Corporation.

Several representative specimens of electric cable were selected that have been degraded through actual nuclear plant service or artificially aged using accelerated thermal and radiation techniques. These aged specimens, together with unaged control specimens, were subjected to a series of demonstration tests using test equipment developed by Indigo Systems. Mr. Elliott Rittenberg, an infrared imaging specialist with IRcameras Northeast, Inc., has been assisting BNL in performing the cable testing. Ultrasound/infrared imaging test equipment will be set up at the BNL cable testing facility to conduct developmental testing and parametric studies using the technique.

TECHNICAL PROGRESS & RESULTS:

During FY 2003, demonstration testing was successfully performed on radiation cross linked polyethylene (XLPE) insulated cables and ethylene propylene rubber (EPR) insulated cables that had been aged to simulate 0, 20, 40, and 60 years of nuclear plant service. The technique was able to indicate cracks and defects in the cable insulation, including those not visible to unaided visual inspection. The ultrasonic probe, when applied perpendicular to the surface of the insulation and the copper conductor, successfully stimulated the cable insulation sufficiently to permit infrared imaging detection of defects more than 12 inches from the point of application. Figure

1 is an infrared imaging thermogram display captured during demonstration testing that shows how the technique indicates the locations (arrows) of hairline cracks in the insulation of an aged nuclear plant cable specimen.

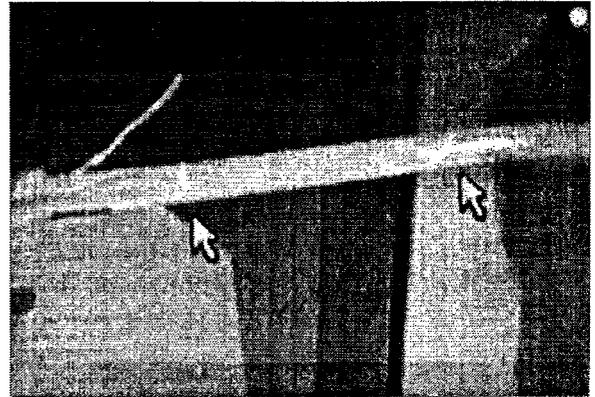


Figure 1. Infrared thermogram display indicating damaged electric cable insulation.

We are negotiating with IRcameras Northeast, Inc. to lease or borrow the ultrasound/infrared imaging test equipment in FY 2004 for use at BNL to conduct the parametric and developmental testing described in the previous section.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$63,000 |
| FY 2004 (budgeted) | \$75,000 |

Application of Compton Suppression Gamma-Ray Spectrometry to Counterterrorism Problems

James R. Lemley

03-072

G. Harbottle

W. Kane

PURPOSE:

Terrorists may use radioactive materials to build nuclear explosives or radiological dispersal devices, so called "dirty bombs." The highest sensitivity radiation detectors being deployed in counterterrorism applications are subject to false alarms caused by radioactive materials that are naturally occurring or are used in medicine and legitimate commercial applications. Background suppression technology coupled with high-resolution gamma-ray spectrometry can detect radiation near background level and reduce false alarms by distinguishing materials with legitimate commercial or medical applications from material intended for malevolent use. This work will demonstrate that background reduction technology combined with high-resolution gamma-ray spectrometry can be used under field conditions for two different objectives. One objective is field identification of radiation signatures in small environmental-monitoring samples without sending the samples to a specialized laboratory for analysis. A second objective is to evaluate whether a Compton anticoincidence shield coupled with a commercial high-resolution gamma-ray spectrometer could be a lightweight alternative that is more convenient for field use in homeland security applications than a spectrometer equipped with shielding made of heavy metal. Procedures will be developed so that personnel with only moderate technical training can operate these instruments effectively.

APPROACH:

We use a threefold approach, drawing on assets currently available at BNL. 1. A Compton suppression gamma-ray spectrometer in the Chemistry Department is being used to establish the conditions for obtaining spectra of materials of counterterrorism interest with the greatest sensitivity and lowest background. This instrument has a germanium well detector surrounded by the Compton shield and is particularly suitable for analyzing small samples containing traces of materials of interest. After establishing the usefulness of this instrument for counterterrorism applications, the goal is to establish the design basis for a similar portable instrument equipped with modern, miniaturized electronics and a physically more robust anticoincidence shield made of bismuth germanate (BGO). A field-usable instrument would eliminate the need to send samples to a specialized laboratory for analysis. 2. A simple method for separating the radium fraction from any one of four uranium decay chains is used to obtain greater sensitivity and specificity in gamma-ray spectra for very small uranium samples. This method could be employed in non-laboratory field conditions on small samples of interest. 3. We are exploring the utilization and adaptation of a commercially available instrument, the Canberra In Situ Object Counting System (ISOCS) gamma-ray spectrometry system for counterterrorism purposes. It was developed for use in the decontamination and decommissioning of facilities, but it can be modified to analyze and interpret spectra obtained from isotopes of interest in the counterterrorism area. BNL has two of these systems; it is significant that several thousand more are already functioning in the nuclear industry nationwide. We plan to borrow a new portable gamma-ray spectrometer with an onboard movable-screen computer to test with the new Compton shield that has been ordered and compare the performance of this lighter weight system with that of the ISOCS.

TECHNICAL PROGRESS AND RESULTS:

The Experiment Safety Review (ESR) (1.3.5) process has been completed so that the necessary radioactive materials can be used with the various instruments. The Compton suppression gamma-ray spectrometer has been refurbished, checked out, and put back into operation. This includes evaluation and adjustment of the photomultiplier tubes on the Compton shield, replacement of inoperable units, and evaluation of the HPGe well counter and timing circuits. We have recorded many spectra and reestablished the complex efficiency vs. energy curve, fitting it mathematically and programming a small computer to calculate unknown values. Dave Alburger, who originally created the system, has rendered major assistance in restoring it to working order. We also thank Kathy Kolsky for preparing quantitative radioactive multi-isotope standards for use with this instrument.

We arranged with Paul Kalb and Larry Milian to use an ISOCS system acquired for the waste management program and measured spectra of common materials containing natural radioactivity that might obscure the presence of special nuclear materials.

Canberra has demonstrated at BNL a new prototype, portable gamma ray spectrometer with onboard computer processing of spectra and special algorithms for the recognition of malevolent radioactivity (improvised nuclear explosives and "dirty bomb" materials). We have ordered a Compton shield employing BGO crystals that will fit this spectrometer as well as high-purity germanium detectors that BNL already possesses. We have met with

the Instrumentation Division and discussed perfecting a miniaturized design for the Compton-suppression electronics and integrating it with the computer control and data acquisition software.

Supplies for micro chemical separation of radium isotopes have been acquired, and the separation procedure has been tested.

To test the capabilities of the Compton suppression system, and as an exercise in studying possible field uses of the new detector, we have acquired four plutonium nitrate specimens (100 micrograms each) having differing isotopic compositions and will participate in a multi-laboratory blind examination of these reference materials. The Institute for Reference Materials and Measurements (IRMM) at Geel, Belgium, prepared the reference plutonium materials for this intercomparison. The plutonium spectra are complete and are being processed. We will be able to compare our results with those of other participants.

SPECIFIC ACCOMPLISHMENTS:

The Detection of the Illicit Movement of Nuclear Materials by Means of High-Resolution Gamma-Ray Spectrometry, Lemley, J., Harbottle, G., and Kane, W., Institute of Nuclear Materials Management 44th Annual Meeting, Phoenix, AZ, July 13-17, 2003.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$125,000 |
| FY 2004 (budgeted) | \$125,000 |

Real-Time Consequence Assessment System for Atmospheric Terrorist Events in the Northeast Urban Corridor

R. Michael Reynolds

03-077

PURPOSE:

Brookhaven National Laboratory, in collaboration with the Department of Energy's Environmental Measurements Laboratory (EML) in Manhattan, is to establish a long-term, urban meteorological measurement program in the vicinity of King Street and Varick in the West Village section of New York City. This study will give BNL an important presence in NYC and lead to the acceptance of an Urban Atmospheric Observatory (UAO) concept by city and federal agencies.

APPROACH:

The approach followed in this program needs to pay attention to the dual goals of the effort: to demonstrate an ability to make long-term meteorological measurements in Manhattan and for the concept to become recognized as the approach for the development of the needed tools for emergency response in the event of a sudden release of contaminants in the urban atmosphere. Towards this end we formed a scientific team with the leading urban scientists in the country: Robert Bornstein, San Jose State University; Steve Hanna, Harvard; and Tim Oke, University of British Columbia. We established a collaborative partnership with Bruce Hicks, National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory, and Sam Lee, EML.

TECHNICAL PROGRESS AND RESULTS:

We installed four sonic systems on the rooftop and sides of the EML building. Each of these instruments produces 48 MB per day which translates to 6 GB per month for the four systems. The instruments collected data at 10 Hz which was more than sufficient to define the fully turbulent flow. The instruments worked very well, and the data recovery amounted to better than 99%. Preliminary data analysis demonstrated a strong double gyre circulation in the King Street Canyon, especially for winds normal to the building. Vertical wind differences between the top floor (12th floor) and 8th (floor) were often as much as 2 m/s, a considerable differential.

In July, a borrowed Sound Detection and Ranging (SODAR) was deployed on the EML roof. Scientifically, these measurements have produced a highly unique data set. When we remove the stations at the end of January, we will have taken almost a complete year of turbulence data in a deep NYC urban canyon. This data set will provide extremely useful information on seasonal variations in the circulations above the city, over the rooftop, and in the canyon.

The SODAR likewise provided an excellent look at the winds well above the building. The EML building is approximately 55 m high, and the SODAR measures winds each 5 m to a height of 50-75 m above the roof. Thus, it doubled the building height and reached well above the turbulent wake over the top of the building.

This work will be continued as part of a study of contaminant dispersion in the streets around Madison Square Garden entitled "The Urban Deep Canyon Study" (UDCS-04) which is planned for the spring

of 2004. We will deploy turbulent instrumentation both on rooftops and on locations at street level such as utility poles and building setbacks. NOAA will contribute turbulent systems on rooftops. A parallel LDRD examines the proof-of-concept exercise using the perfluorocarbon tracers (PFTs) with seven different compounds.

SPECIFIC ACCOMPLISHMENTS:

Overview of UAO Pilot Program: Instrumentation and Future Plans. R. Michael Reynolds. First Scientific Workshop for the UAO NYC. DHS/EML, NYC, 27-28 January 2003.

Review of the Urban Atmospheric Observatory (UAO). R. Michael Reynolds, Workshop Review of Sensor Technology for the Battelle Labs, ORNL, March 05, 2003.

New York City Urban Atmospheric Observatory, Sam lee & R. Michael Reynolds, Seventh Annual George Mason University Transport and Dispersion Modeling Workshop, Fairfax, Virginia, June 17-19, 2003

An Urban Atmospheric Observatory For New York City, R. M. Reynolds, R. D. Bornstein, T. R. Oke, S. R. Hanna, R. Michael Reynolds, StevFifth International Conference on Urban Climate (ICUC-5), Lodz, Poland, September 1-5, 2003.

NYC Urban Atmospheric Observatory (UAO). R. Michael Reynolds, Urban Dispersion Model Working Group (UDMWG) Meeting, Dugway Proving Ground Salt Lake City Conference Center, September 22-23, 2003.

NYC Urban Atmospheric Observatory (UAO). R. Michael Reynolds. DCNet Advisory Group meeting, Washington, DC, October 10, 2003.

We have strong assurances from the Defense Threat Reduction Agency (DTRA) that funding for as much as \$500K will be provided to significantly increase the scope of the study.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$69,765 |
| FY 2004 (budgeted) | \$73,000 |

Application of Thin Film-Like Dosimeters for Port Security and Anti-Terrorism

E. Kaplan

03-081

PURPOSE:

To evaluate the feasibility of using an inexpensive, passive integrating dosimeter sensitive to neutron radiation for the purpose of detecting radioactive materials concealed in cargo containers or on board ships.

Expected technical results and its technical implications (feasibility): To demonstrate feasibility of integrating existing components (a bubble detector sensitive to neutrons and an electronic system comprised of GPS (global positioning system), self-configuring network and remote 2-way communications) into an inexpensive miniaturized package that can signal the presence of radioactive material in shipping containers while in transit (e.g., on container ships). Of particular interest are nuclear explosives, either diverted weapons or improvised devices (IED), materials from which nuclear explosives could be made and materials that could be used in radiological dispersal devices (RDD).

Implications to BNL: Potential new programs in developing inexpensive miniaturized integrated detector (neutron, gamma, beta, alpha; remote readouts) and their use in a novel system to detect and locate (worldwide) radiation sources in all forms of transportation and storage.

APPROACH:

Background leading to project: Thousands of ships carrying millions of containers call at the port of New York each year bringing

cargo from all parts of the world. Commercially available, passive, radiation-dosimeter materials are inexpensive enough that every shipping container could be equipped with such devices. If an unexposed dosimeter-like device were installed at the beginning of a voyage, it would integrate the radiation-flux to which it was exposed over the duration of the voyage. In principle, greater sensitivity for detection of various types of ionizing radiation should be possible because of the long integration time.

Scope of investigation: Procure and test superheated emulsion (i.e., bubble) detectors using ^{252}Cf sources at BNL. Develop a technique to digitize the response of bubble detectors. Interface bubble detectors with a commercially available real-time, low-cost, low-power, highly secure wireless network system that utilizes low-power radios and radio-frequency identification (RFID) and Real-Time Locating Systems (RTLS) tags. (These are known as asset tracking systems.) Demonstrate system in field tests.

Methods:

1. Develop testing protocols and obtain necessary permits.
2. Procure and test bubble dosimeters.
3. Perform time-distance exposures using TLDs (thermoluminescent dosimeters), CR39 films and bubble detectors.
4. Determine ability of bubble detectors to detect low activity neutron sources over the course of a few days (e.g., at the start of an overseas voyage).
5. Develop procedure to digitize bubble detector response.
6. Interface digitized bubble detector response with commercially available technology to provide instantaneous, worldwide, remote readout and location of suspect containers.
7. Field test integrated system to show feasibility of integrated system.

8. Miniaturize system and show applicability to expanded detection system (e.g., inclusion of other radiation detectors; use by wide range of package/container transporters and couriers, police).

Collaborators: James Lemley, Sylvester Suda, Larry Milian.

TECHNICAL PROGRESS AND RESULTS:

FY 2002: Developed testing protocols, obtained necessary permits and radiation measurement work plan for time-distance exposures. (Note: these activities alone accounted for approximately 40% of first year funding.) Procured two types of bubble detectors (one sensitive to epithermal and thermal neutrons, the other to a range from <200Kev to >15Mev). Calculated expected number of bubbles from background radiation and from ²⁵²Cf sources existing at BNL.

FY 2003: Performed time-distance exposures of TLDs, CR39 films and bubble detectors using two sets of ²⁵²Cf sources. Demonstrated that bubble detectors respond quickly (i.e., over 1-3 days) to low activity neutron sources. Engaged in technical discussions with a bubble detector manufacturer concerning possible future collaboration. Met with developers of WI-FI/GPS system (wireless fidelity/global positioning system) and ascertained ability of this product to interface with bubble

detectors. Discussed possible future collaborations with developers and manufacturer of bubble dosimeters.

FY 2004: October to Present - Visited Canadian manufacturer of bubble detectors to discuss concept of remote worldwide monitoring system. Agreement in principle to cooperate in future development will explore modes of cooperation (e.g., CRADA (Cooperative Research and Development Agreements), SBIR (Small Business Innovation Research)). Initiated technical discussions with manufacturer of commercially available wireless asset tracking system also for possible future collaboration.

FY 2004: Planned - Efforts will comprise of three phases: (1) develop technique to digitize response of bubble detectors, (2) interface digitizer system with commercially available asset tracking system, and (3) perform limited field test to show feasibility of system for use with shipping containers (e.g., using shipping container at BNL).

SPECIFIC ACCOMPLISHMENTS:

Filed record of invention with BNL patent office.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$110,000 |
| FY 2004 (budgeted) | \$113,000 |

Novel Xenon Detector Concepts for Homeland Defense

Peter Vanier

03-083

G. Smith

D. Makowiecki

PURPOSE:

This project will explore a number of novel concepts to enhance the performance of gamma ray spectrometers based on high-pressure xenon. Such detectors have considerable potential for homeland defense applications, as well as for whole-body counting in nuclear medicine. The existing prototype chamber designed and built by BNL's Instrumentation Division has been useful for studying the physics of operation in a simple geometry but is not optimized for a field-operable instrument. A detailed understanding of the factors limiting detector performance will be needed in order to design and construct large volume prototypes for stand-off detection of special nuclear materials and radiological dispersal devices.

APPROACH:

This project builds on previous experience in high pressure noble gas radiation detectors. The method is to construct an ionization chamber containing a sufficient mass of compressed xenon to absorb gamma rays with energies up to 3 MeV. The resulting cloud of ionized electrons drifts in a moderate electric field to a Frisch grid and passes into a high-field region to be collected at an anode. A sensitive preamplifier detects the motion of the charges moving a fixed distance from the grid to the anode, and a pulse shaping amplifier produces a signal corresponding to the energy of the gamma ray absorbed. This

signal is digitized and stored in a spectral histogram.

The project aims to make significant improvements in the state of the art by means of new geometrical designs of the ionization chamber and its electrodes as well as the pulse-processing electronics.

The operational parameters that are considered crucial are the energy resolution of the detector and its absolute efficiency as a function of energy. These factors determine whether a particular source can be detected and identified as a threat in a given time. Other considerations that affect the applicability of the technology to specific tasks include portability, ease of operation, power consumption, and durability.

Aleksey Bolotnikov, widely recognized as an expert developer of xenon spectrometers, was hired.

TECHNICAL PROGRESS AND RESULTS:

A completely new design of the electronics package for the existing xenon spectrometer was constructed (see Figure 1). The high voltage power supply was replaced with a compact programmable unit controlled by a custom-built microprocessor board. This charging system was programmed to apply the appropriate potentials to the internal components of the chamber periodically and then disconnect the ripple of the power supply during data acquisition periods. A large mechanical relay was replaced with a miniature switching device. The bulky utility box containing batteries, high voltage power supply, and a commercial multi-channel analyzer was eliminated by using more compact modules enclosed in the box containing the xenon chamber. This reconstruction improved the portability and

ease of operation, with a single switch to turn on the instrument, rather than a number of connections and adjustments to be set up.

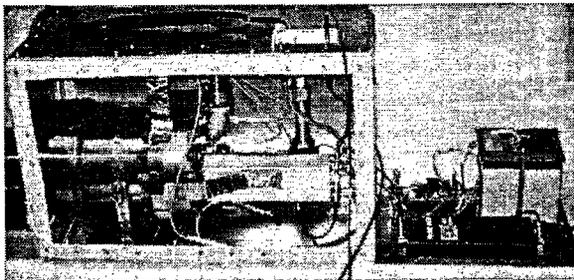


Figure 1. Xenon spectrometer with new electronics package.

Preliminary testing of the reconstructed system has illustrated the benefit of a user-friendly instrument package. The spectral resolution is slightly inferior to earlier published results, and studies are underway to determine if the new system is more susceptible to electromagnetic interference or whether the purity of the xenon in the chamber has degraded over a period of several years. One new component that might have caused peak-broadening was a novel chain of tera-ohm resistors chosen for very low power consumption, but possibly resulting in sub-optimal potential distribution in the chamber.

The creation of software for automatically analyzing the data and comparing unknown spectra to a library of the usual suspects was initiated. The task involves selecting regions of interest, stripping peaks from the continuum, and performing a statistical comparison with stored templates. The success of the method in distinguishing targeted sources from medical isotopes or natural background is critically dependent on the spectral resolution.

Concepts for new and improved ionization chambers (Figure 2) were discussed in some detail with experts in the Instrumentation

Division, and most of the components have been collected for constructing a second detector.

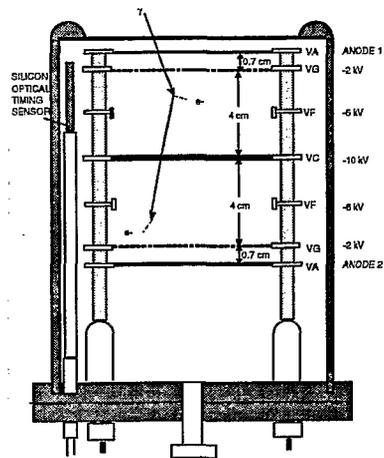


Figure 2. Dual anode concept

In FY 2004, the questions about the performance of the existing detector will be resolved, and it will be made ready for field trials with easy-to-operate automated software. If necessary, the xenon will be re-purified to obtain optimum performance. The construction of a second ionization chamber with a new electrode configuration will proceed.

SPECIFIC ACCOMPLISHMENTS:

Proposals submitted:

DOE/NA-22: "High Pressure Xenon Detector Array," awaiting disposition.

DHS: "High Pressure Xenon Detector Array," Passive Detection section of Radiological and Nuclear Countermeasures Program, DOE Science and Engineering Labs joint proposal, awaiting disposition.

DOE/NA42: "Hand-held Gamma-Ray Search Detector for Rapid Survey," \$100k

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$104,000 |

Defining New Pathways for Disarming Anthrax Toxin

Paul I. Freimuth

03-086

PURPOSE:

Bacillus anthracis, the causative agent of anthrax, secretes a highly potent toxin that can enter human or animal cells and rapidly cause cell death. Anthrax toxin is a complex molecular machine, consisting of three separate protein subunits each of which plays a distinct role in the mechanism of cell intoxication and death. Self-assembly of the three toxin subunits on the outside surface of human or animal cell membranes is the obligatory initial step of the intoxication mechanism. The existing vaccine induces antibodies, which bind to one of the toxin subunits and block self-assembly of the active toxin protein complex. Although the vaccine effectively protects against subsequent infection, it is not effective as a therapeutic agent because of the very rapid progression of disease in infected individuals. Therefore, antidotes or other disease-blocking strategies must be developed for effective treatment of anthrax infection in unvaccinated individuals. The goals of this project are to elucidate how one of the toxin subunits, the "lethal factor" metalloproteinase, enters the cytoplasm of target cells and how lethal factor (LF) recognizes and proteolytically digests proteins within the target cell cytoplasm. Our results may provide the foundation for future development of antidotes that block assembly of active toxin on the surface of target cells, interfere with cellular uptake of LF, or inhibit proteolytic digestion of protein substrates by LF.

APPROACH:

Earlier studies described the general molecular features and activities of the three toxin subunits, culminating in the determination of

near-atomic resolution structures of the subunits by X-ray crystallography. Although we now have a detailed picture of the toxin molecule, its mechanism of action still is not well understood. For example, the LF subunit is known to have zinc-dependent metalloproteinase activity, but the actual protein substrates that are destroyed by LF and lead to death of human cells are not known. LF has been shown to digest one particular protein kinase *in vitro*, but other studies have shown that inhibition of this kinase does not compromise cell viability. Furthermore, the rate of hydrolysis of this kinase substrate by LF is much slower than the typical rate of substrate digestion by other proteases such as trypsin, suggesting that other human proteins may be much more sensitive to digestion by LF.

LF and the other toxin subunits normally are secreted from *B. anthracis* cells. However, several investigators reported that LF also can be produced as a recombinant protein in *Escherichia coli* and further that LF can be modified to block its secretion and sequester it in the *E. coli* cytoplasm. We expressed this truncated, sequestered form of LF in *E. coli* for our experiments. In addition to the intact LF protein, we unexpectedly observed that a small fragment derived from the N-terminal region of LF also accumulated in the *E. coli* cytoplasm. This smaller fragment was not observed in *E. coli* cells expressing LF mutants that have disrupted enzymatic activity. On the basis of these results we proposed that the LF protein digests itself when it is sequestered in the *E. coli* cytoplasm.

As noted above, the first step in intoxication is the self-assembly of LF and other toxin subunits on the outside surface of target cells. It is generally believed that LF subsequently dissociates from the other toxin subunits to reach the cytoplasm of human target cells, but the mechanism for LF dissociation has not been determined. Diphtheria toxin, which also initially self-assembles as heterodimers on the cell surface, is known to release its active

subunit into the target cell cytoplasm through an auto proteolytic mechanism. Therefore, it seemed possible that auto proteolysis also could be the mechanism for delivery of LF to the target cell cytoplasm. Furthermore, characterization of the site in LF that is cut by auto digestion might provide insights into the identity of additional human proteins that are efficiently cleaved by LF during cell intoxication. Therefore, we focused this research project on characterization of LF auto proteolysis.

TECHNICAL PROGRESS AND RESULTS:

Our major objective this past year was to acquire data, which demonstrated conclusively that LF indeed cleaves itself by an auto proteolytic mechanism. We attempted to resolve this issue by acquiring both genetic and biochemical evidence. As noted above, the product of auto digestion was not apparent when LF mutants that have amino acid changes in critical active site residues were expressed in *E. coli*. Upon more careful examination, however, we observed that degradation products did in fact appear, but the molecular weights of these products as measured by gel electrophoresis differed from the product that was generated in *E. coli* cells that expressed the wild-type LF enzyme. This genetic analysis thus did not allow us to conclude with certainty that the degradation resulted from auto proteolysis and not from digestion by an *E. coli* protease.

We attempted to resolve this issue by biochemical analysis. Wild type LF and active site mutants were purified to homogeneity from *E. coli* cell homogenates by affinity chromatography and size exclusion chromatography and were incubated in vitro under conditions reported to support digestion of other standard substrates (e.g. peptides derived from the above-mentioned protein kinase). No auto digestion products were observed. LF cleaves the human kinase protein within a conformationally disordered,

flexible region. We speculated that LF may preferentially cut other protein substrates, including itself, within regions that have a similar high degree of conformational flexibility. We confirmed this model by showing that LF was able to digest a fusion protein that we constructed which had a 15-residue peptide derived from the LF protein fused to the C-terminus of a stably folded carrier protein. The site of digestion of this artificial substrate corresponded precisely to the site that is cleaved during apparent auto proteolysis of LF within *E. coli*. Thus we now have solid genetic and biochemical evidence for LF auto proteolysis. We conclude that LF may only be susceptible to auto proteolysis for a brief period, during while it is folding into its native conformation in *E. coli* cells. This would imply that many human proteins also might be susceptible to digestion by LF while they are folding or being synthesized on ribosomes.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$100,000 |

Structural Studies on the Integral Membrane Protein AlkB

John Shanklin

03-094

PURPOSE:

The goal of this LDRD proposal is to initiate structural studies on the Alkane ω -hydroxylase (AlkB) from *Pseudomonas oleovorans*, exploiting its unique structural organization that is ideally suited to both crystallography and cryo-electron microscopy.

APPROACH:

Approximately 30 percent of all proteins reside in membranes and with a few notable exceptions little is known about their structures and how those relate to their function. There are two major obstacles to structure determination of membrane proteins: 1) Membrane proteins exist in a lipid bilayer along with many other membrane proteins, which greatly complicates purification because they are all functionally tethered together in the same membrane. 2) Solubilizing proteins from a complex heterogeneous membrane environment while maintaining functional protein requires precisely defined conditions that are specific to each protein. The solution to this complex problem is difficult, because to purify membrane proteins, they must first be solubilized, and the conditions for solubilization often interfere with the conditions needed for purification. A unique property of AlkB is that it forms homogeneous protein vesicles that can be purified in the absence of detergents. This offers a unique opportunity to simplify the obtaining of structural information for this particular integral membrane enzyme.

A Postdoctoral Research Associate, Mary Lynn Baniecki, started work in this lab in April 2003.

TECHNICAL PROGRESS AND RESULTS:

Progress to date has been rapid. Successful efforts to purify AlkB for structural work depends on having a fast and accurate assay for AlkB. To do this we first needed to assemble and verify an assay. The AlkB enzyme is the terminal electron acceptor of a three-component electron transport chain comprising a flavoprotein rubredoxin NADP(H⁺) oxidoreductase, and a 2Fe, 2S iron sulfur protein rubredoxin. We determined that the spinach ferredoxin NADP(H⁺) oxidoreductase could substitute for the rubredoxin reductase, but rubredoxin had to be over expressed and purified for our experiments. Ferredoxin NADP(H⁺) oxidoreductase and rubredoxin were both over expressed in *Escherichia coli* and purified sufficiently to generate assay component cofactors to allow spectroscopic assay of AlkB activity. The assay was validated using crude AlkB preparations. A major portion of the report period was spent systematically investigating the expression of AlkB in *E. coli*. The expression conditions we focused on were *E. coli* host, growth media, aeration and temperature at different phases of growth. The *Pseudomonas* AlkB was introduced into several different heterologous hosts, i.e., strains of *E. coli* that were documented to have different desired properties with respect to expression of different proteins. Factors affecting the expression of membrane proteins are not well understood. Thus, trial and error is the standard protocol for optimizing expression host. Several hosts were tested, including BL21, BL21 gold, BL21pLysS, C41 and C43. Interestingly, C41 and C43, cell lines designed to increase expression of

membrane proteins, did not seem to offer advantages over the standard BL21 cell line. On the other hand, as judged by SDS-PAGE (Sodium Dodecyl Sulfate-PolyAcrylamide Gel Electrophoresis) analysis, BL21pLysS did offer both stronger expression and more protein in the ultra supernatant, fulfilling our criteria for membrane integration. We discovered that AlkB has a tendency to auto induce, that is it expresses inappropriately. In addition to adventitious expression, it tends to produce a truncated protein that forms inactive inclusion bodies. Thus, under unfavorable conditions, the AlkB tends to be produced in a form that is useless for purification and structural studies. We focused on two media in particular, LB and TB, with several pHs. LB is a rich media, and TB is a less rich media. We observed that in the richer LB media, the tendency to form inactive AlkB was enhanced. We did similar analyses on oxygenation, controlled by shaker platform rotation speed and by temperature of pre-induced growth and induced growth. Our experimental data suggest that auto-induction to produce inactive protein results from poorly oxygenated cultures grown at 37C and that growth of AlkB in TB pH 7.3 at 30C with rapid shaking (275 RPM) using baffled 2.8 liter flasks provided the best solution to produce cell material best suited for purification. Several small-scale AlkB purifications were attempted that produced active protein. The challenge now remains to scale up the process to increase yields to

the point that we can start detergent solubilization trials. We also plan on attempting to express the protein with an affinity tag such as hexa-histidine to allow trials of protein purification using Ni-NTA affinity chromatography.

In summary we established:

- Purification of ferredoxin NADP(H⁺) oxidoreductase and Pseudomonas rubredoxin in sufficient quantity and quality for assay development.
- Development of an assay with appropriate sensitivity and linear dynamic range for biochemical characterization of purification steps of AlkB.
- Development of culture conditions, AlkB in pET3a, in host BL21DE3pLysS in TB, pH 7.3 in baffled 2.8 liter Fernbock flasks shaken at 275RPM at a temperature of 30C until induction, followed by temperature increase to 37C after induction with 0.4mM IPTG.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$ 52,754 |
| FY 2004 (budgeted) | \$ 98,000 |

Roles of Dopamine Receptor Agonists in Brain Metastasis of Breast Cancer

Xinhua Lin

03-098

PURPOSE:

A hallmark of cancer is pathological angiogenesis, without which tumors will not grow beyond a critical size or metastasize to other organs. Thus, the angiogenic vessel in tumor tissue is a very attractive target for both therapy and diagnosis. The purpose of this project is to adapt and establish an animal model for breast cancer brain metastasis, evaluate the roles of angiogenesis in brain metastasis and study the effects of antiangiogenic pharmacological intervention on brain metastasis based on the targeting of dopamine receptors in angiogenic capillary endothelial cells.

APPROACH:

Preclinical and clinical data suggested that antiangiogenic approaches might be an effective means to control tumor metastasis. Most of the antiangiogenesis treatments target the endothelial cells of the newly formed tumor vessel or inhibit the action of proangiogenic molecules such as VEGF (Vascular Endothelial Growth Factor). Dopamine, a catecholamine neurotransmitter, recently has been the focus of the attention for its newly discovered antiangiogenic effects. Dopamine and related molecules have been shown to inhibit the growth of cancer cell growth in vitro and tumor growth in vivo -- notably spontaneous mammary tumors. Moreover, endothelial cells from VEGF-induced neovasculature are strongly positive for D2 receptor, whereas endothelial cells from normal vessels are weakly positive or negative. The differential expression of D2

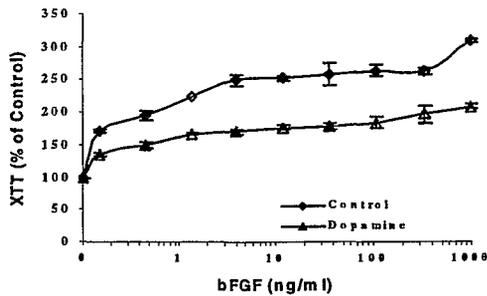
receptor led us to hypothesize that it can be a target for antiangiogenic treatments and also a potential target for imaging tumors. To test these hypotheses, expression of angiogenesis markers (endosialin, VEGFR [VEGF receptors] and dopamine receptor) in brain metastases will be examined. The binding kinetics of D2 ligands and tumor vessels will also be examined in order to determine whether preexist tracers for D2 receptor can potentially be used as tracer specific for tumor vessel.

This project is designed to utilize and compliment the existing expertise at BNL in brain tumors, dopamine neurobiology, and neuroimaging. It is also designed to generate valuable scientific models and data irrespective of whether the hypotheses are fully borne out. Finally, this project is designed to address an area of significant biomedical importance in a way to attract future extramural funding from a variety of federal and private extramural funding agencies.

TECHNICAL PROGRESS AND RESULTS:

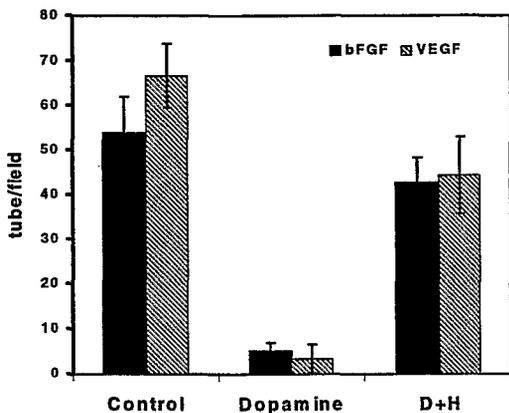
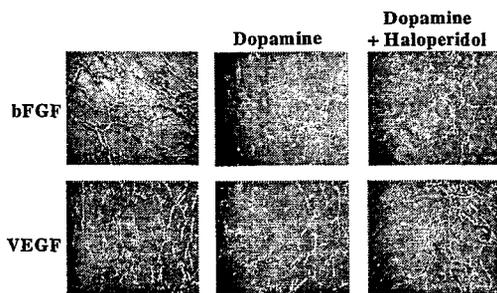
Dopamine inhibits growth factor-induced cell proliferation in endothelial cells:

We found that dopamine inhibits growth of bFGF-induced in bovine aortic endothelial cells in physiological concentration. At this concentration dopamine counteracts a wide dose range of bFGF's action (up to 1000 ng/ml), whereas it produces no lethality to resting endothelial cells (see figure below). This finding proved the concept that catecholamine neurotransmitter could potentially inhibit angiogenesis.

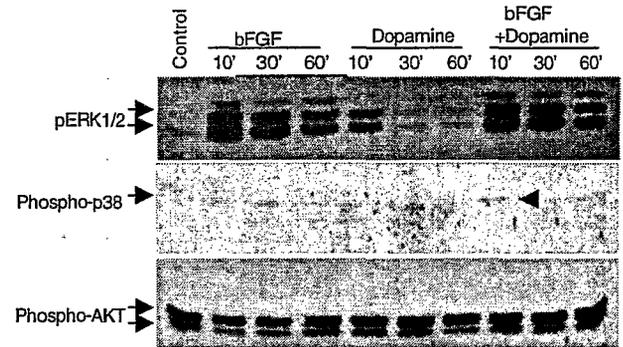


Dopamine inhibits growth factor-induced angiogenesis in vitro.

Using an in vitro angiogenesis model, we demonstrated that dopamine suppresses angiogenesis induced by bFGF or VEGF. Further, a D2R antagonist haloperidol reversed the suppressive effect of dopamine, indicated that the effects of dopamine is mediated by dopamine D2 receptor (see figure below).



Dopamine activates p38 MAP kinase and might be the one of the molecular mechanisms of its inhibitory effects.



To identify molecular targets for the anti-angiogenic effect of dopamine receptor agonists, we hypothesized that dopamine treatment activates p38 MAP kinase in endothelial cells and the p38 activation plays a role in the dopamine receptor agonist-induced anti-angiogenic effect. Using rat microvascular endothelial cells (RMECs) as models, we found that Endothelial cells expressed very low basal activity of p38. Treatment of bFGF or dopamine alone did not induce p38 activity (see figure below). Increased p38 activity was observed in the cells treated with both bFGF and dopamine (black arrow). bFGF-induced ERK1/2 MAP kinase activity and AKT activity were not affected by dopamine treatment indicating that the change in p38 is specific.

These findings formed the base of a manuscript describing D2R agonist as an anti-angiogenic agent, and also set the stage for the subsequent investigations in FY 2004 including: i) testing the differential expression pattern of D2 receptor in endothelial cells in vitro and in vivo, ii) studying the binding between D2 agonist and D2R on endothelial cells to validate whether D2 receptor is a suitable target for noninvasive imaging of brain metastasis.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$100,000 |

The MicroPET Study of Gene Expression in Rodents

Panayotis Thanos

03-099

PURPOSE:

The chief objective of this research is to develop methods and assess the potential of microPET for the investigation of the function of genes in the whole organism. We specifically propose to assess the function of specific genes in the brain of rats, in which we will over express the gene in specific brain areas and in mice, in which through knock out or knock in technology, these genes have been deleted or modified. The implications of these results would be critical in furthering our understanding in several research areas currently at BNL: a) substance abuse, b) aging, c) neurodegenerative disease, d) learning and memory, e) cancer, and f) radiation. More specifically these results will be critical in soon-to-begin studies of radiation exposure and treatment of neurodegenerative disease with stem cells.

APPROACH:

Rapid developments in genetic research have given rise to the new field of behavioral genetics and a growing demand for assessing in-vivo the expression and function of genes, as well as, how they correlate with environmental factors and behavior. Recent PET studies have started to link disease associated genetic mutations with specific brain metabolic and biochemical abnormalities that occur prior to disease presentation (Feigin et al., 2001; Matsuda, 2001). These studies have highlighted the potential of PET as a tool to investigate the consequences of genetic polymorphisms in regional brain function. Mice, through the use of "knock out" and

"knock in" technologies, have been particularly valuable in elucidating the role of genes and the proteins they encode in behavior and drug effects. This model is valuable in predicting the genotypic basis of neuropsychiatric disease.

MicroPET technology is a new and exciting area of research. The present research examines the development of methods assessing the feasibility and sensitivity of microPET in genetically engineered mice and genetically modified rodents. We are evaluating the genes involved in brain dopamine (DA) neurotransmission [D2 receptor and DA transporter (DAT)] since this is a system for which we have access to appropriate radiotracers and to transgenic and knock out animals. Finally, methods employed include microPET and autoradiography.

Collaborators include: Dr. G. J. Wang, Dr. J. Fowler, and Dr. S. J. Gatley.

TECHNICAL PROGRESS AND RESULTS:

(1) Measured dopamine receptor and transporter levels in transgenic mice in: (a) D2 wild type, D2 heterozygous and D2 knock out and (b) DAT wild type, DAT heterozygous and DAT knock out. (2) Measured D2 levels in rats that have regional overexpression of these molecule targets. (3) Evaluated the sensitivity of microPET to assess functional brain changes as measured by regional brain glucose metabolism in D2 family transgenic mice that are treated with the psychostimulant MP. For next fiscal year, the following milestones are planned: (1) Evaluate the sensitivity of microPET to assess functional brain changes, as measured by regional brain glucose metabolism in rats with regional overexpression of DAT, who are treated with a DAT blocker drug. (2) Evaluate the

sensitivity of microPET to assess functional brain changes, as measured by regional brain glucose metabolism in Transgenic DAT, transgenic mice that are treated with DAT blocker drugs.

This project involves animal vertebrate subjects (rodents).

SPECIFIC ACCOMPLISHMENTS:

Thanos, P. K.; Taintor, N. B.; Rivera, S. N.; Umegaki, H.; Ikari, H.; Roth, G.; Ingram, D. K.; Hitzemann, R.; Fowler, J.; Wang, G. J.; and Volkow, N. D. DRD2 Gene Transfer into the Nucleus Accumbens of the Alcohol Preferring (P) and Non Preferring (NP) Rats Attenuates Alcohol Drinking: A behavior & microPET study. Alcohol Clin Exp Res. 2003 (in Press).

Ding, Y. -S.; Gatley, J.; Thanos, P. K.; Shea, C.; Garza, V.; Xu, Y.; Carter, P.; King, P.; Warner, D.; Fowler, J. S.; and Volkow, N. D. Is the *l-threo* Enantiomer of MP (Ritalin) Inactive in the Brain when the Drug Is Given Orally? J Nucl Med (in Press). (2003).

Alexoff, D. L.; Vaska, P.; Marsteller, D.; Li, J.; Logan, J.; Fowler, J. S.; Taintor, N. B.; Thanos, P. K.; and Volkow, N. D.

Reproducibility of ¹¹C-Raclopride binding in the rat brain measured with the MicroPET R4: Effects of photon scatter and tracer specific activity. J Nucl Med. 44(5): 815-822. (2003).

Thanos, P. K.; Taintor, N. B.; Alexoff, D.; Vaska, P.; Logan, J.; Grandy, D. K.; Fang, Y.; Lee, J. H.; Fowler, J. S.; and Volkow, N. D. In Vivo Comparative Imaging of Dopamine D2 Knockout and Wild Type Mice with [¹¹C] raclopride and microPET. J Nuclear Medicine. 43(11): 1570-1577. (2002).

Thanos, P. K.; Rivera, S. N.; Grandy, D.; Rubinstein, M.; and Volkow, N. D. Acute Administration of Methylphenidate in Dopamine D4 Transgenic Mice: Effects on Locomotor Activity, Conditioned Place Preference and Brain Metabolism using FDG microPET. Society for Neuroscience Annual Meeting, New Orleans, LA, Nov 6-12, 2003.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$ 50,000 |
| FY 2004 (budgeted) | \$100,000 |

Investigation of the “Early Response” in Functional MRI

Thomas Ernst
L. Chang

03-100

PURPOSE:

Functional magnetic resonance imaging (fMRI) allows the non-invasive observation of brain activation. Although fMRI has had an enormous impact on the study of cerebral activation, its dependence on vascular events has certain disadvantages. For instance, the vascular response has a latency of 2 to 3 seconds after stimulus onset; this delay is one to two orders of magnitude slower than the time scale of many physiological processes. The slowness of this vascular response is unfortunate because ultrafast MRI can achieve a time resolution of 100 ms. The ability to observe not only the spatial but also the temporal aspects of cerebral activation, with a time resolution of 100ms, would magnify the already enormous impact of fMRI on the understanding of brain function.

The purpose of this study is to further study a small signal that can be detected with functional fMRI within 500 milliseconds after a stimulus. This small signal is called the “early response.” The early response may provide an accurate location of brain cells that are using oxygen. This research may make it possible to observe not only “where” brain activity is occurring but also “when” it is occurring.

APPROACH:

We propose to develop techniques and scan 60 normal subjects to answer three questions: 1) whether we can see the “early response” more clearly before the BOLD (blood-oxygenation-level-dependent)

response starts, 2) whether signal changes in the large blood vessels will affect the early response, 3) whether a contrast agent (gadolinium) that stays within the blood vessels will affect the early response. There will be two phases of the protocol. For phase I (technical development), we will recruit up to 20 subjects for the fMRI study. For phase II, we will recruit 40 subjects, who will have 2 fMRI study sessions.

TECHNICAL PROGRESS AND RESULTS:

Phase I of the project required significant technical developments, which are now completed. First, a computer movie was created which shows a flickering checkerboard to stimulate the visual cortex. Given the transient nature of the “early response,” software was written to precisely synchronize the movie with the MRI data acquisition. Several versions of the movie were created to pseudo-randomize the starting time of the movie in order to minimize practice effects.

A software package was written (in IDL, or “interactive data language”), that allows a flexible and direct analysis of the fMRI data sets acquired.

The MRI data acquisition parameters for the “early response” experiments were optimized. The final echo planar imaging (EPI) sequence has a time resolution of 500ms, achieves a signal-to-noise ratio (or SNR) above 100 for a single shot EPI scan, and allows acquisition of 10 slices, each 5 mm thick with 1 mm gap. A surface coil is being constructed to further improve the SNR. Significant effort was put into elimination of noise sources in the MRI scanner, such as the waveform generators and gradient amplifier overheating; this is important due to the smallness of the “early response” signal. The existing scan

reconstruction software was modified to minimize the effect of global signal changes.

At this point in time, 13 human subjects have been recruited into phase I of the project. Some of these subjects were scanned to optimize the scanner sequence (see above), whereas the more recent subjects were presented with the flicker-board stimuli. The data from these preliminary studies are being evaluated. The "early response" seems to be detectable in most of the subjects. Once the reliability of these experiments has been established, phase II will be initiated to assess the

physiological mechanisms underlying the "early response."

This project involves human subjects.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$240,000 |
| FY 2004 (budgeted) | \$251,000 |

PET Imaging of Violent Behavior

Gene-Jack Wang

03-101

PURPOSE:

Violence is one of the most pressing social problems in the U.S. and in the world. The mechanisms leading to violence are complex and multifactorial and are poorly understood. The interaction of neurobiological and environmental factors plays an important role in the development of violent behavior.

APPROACH:

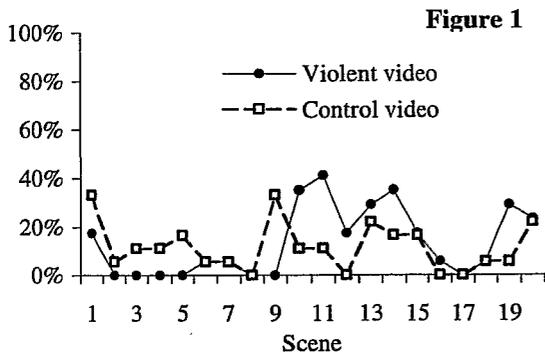
Research on exposure to television and movie violence suggests that viewing of violence increases aggressive behavior. High trait aggressive individuals enjoy viewing violent videotapes more than do low trait aggressive individuals. Videotape violence is more likely to increase aggression in subjects who enjoy violent scenes than those who do not. We will investigate the possibility of using PET technology to understand the role brain circuits play in non-aggressive and aggressive behavior. We will assess the effect of aggressive/violent (R-rated) video presentation on glucose metabolism in healthy male subjects.

TECHNICAL PROGRESS AND RESULTS:

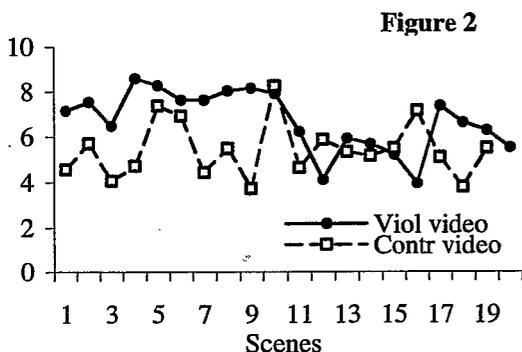
Protocol approval for human study: For the proposed human research project, we first submitted a research proposal entitled "Brain metabolic response to images of violent behavior" to the institutional Review Board (IRB) on 11/22/02. The protocol was approved by IRB (#381) on 7/1/03 and by the Clinical research center (CRC) on 8/22/03. In this study, we assessed the involvement of the limbic system and the frontal cortex using PET and F-18-fluorodeoxyglucose (FDG) as a tracer to measure brain metabolic responses after

viewing an R-rated video, a control video and at baseline (no video) on 3 different days. The order of the study days were varied across subjects and the order of conditions were randomized. The video presentations started 10 minutes before the FDG injection and continued during the time of tracer uptake for a total of 40 minutes. The PET scans started at 35 minutes after the FDG injection.

Video presentation: 1) *Production of the video:* Two videos were edited from movies and documentary films for the project. One video contained 20 scenes of aggressive or violent acts (e.g. domestic violence, murder, street fight) for a total of 40 minutes. The 40-minute control video contained 19 peaceful scenes (i.e. people interacting, sports). The length of the scenes were between 1-4 minutes. The level of intensity of video scenes were arranged to meet the dynamic of radiotracer uptake. We kept the level of action and interest of the videos constant throughout the presentation and kept the length, recognition and intensity compatible with the corresponding scene in the presentations. 2) *The survey for the videos:* To assess if the quality of videos met the goal of the project we conducted a survey of 17 coworkers (10 male and 7 female) of the PET group before starting the proposed project. The coworkers were asked to rate their recognition of the video and assess the level of intensity, action and interest after viewing each scene of the videos. The scale of the ratings was set at 10 as the most and 1 as the least. 3) *Results of the survey:* The levels of recognition of the selected video scenes in both violent and control videos ranged from 0 to 40% and no significant difference between the videos ($p = 0.6$). The most recognizable scenes were the 11th scene in the violent video and the 1st and 9th scenes in the control video. The 2nd to 8th scenes of both violent and control videos were less recognized (Figure 1).

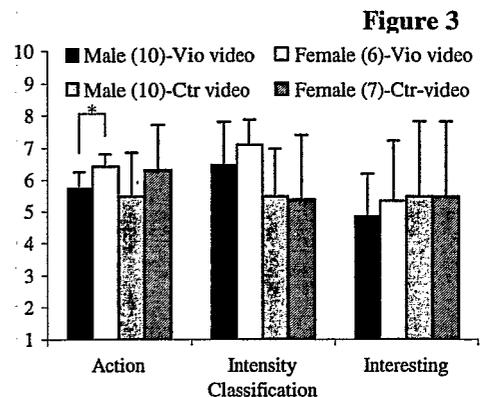


The 4th scene (8.6 ± 1.5) of the violent video and the 10th scene (8.3 ± 1.6) of the control video were rated as the most intense of the videos (Figure 2). The scenes with higher intensity in the violent video were between the 4th and 10th scenes. The intensity of the scenes in the control video were not different throughout the study.



The male coworkers ratings of the levels of action (5.8 ± 0.5 , 5.5 ± 1.4), intensity (6.5 ± 1.3 , 5.5 ± 1.5) and interest (4.9 ± 1.3 , 5.5 ± 1.1) between the violent and control videos were not different (Figure 3). The female (6.4 ± 0.4) coworkers ratings of the scenes in the violent video had more action than the male (5.8 ± 0.5 , $p < 0.007$) coworkers. **4) Interpretation of the survey results:** A few of the scenes in the videos were recognized by the coworkers. However, the level of recognition was not different between the two. The least recognizable and the most intense of the videos were between the 4th and 10th scenes, which were about 2 min prior to and 10 min post FDG injection. It was the optimal time for the FDG uptake in the brain and the evaluation of

brain function. The coworkers rated the videos similar in action and interest. The video presentations met our goal for the project.



PET imaging study: Since IRB and CRC approval, we have screened 15 subjects for the project. Two subjects were selected as "aggression prone" and 4 subjects were selected as "non-aggression prone." The selection was based on the study of physician and psychologist evaluations of the subjects' responses to psychological questionnaires and their responses to a brief R-rated video presentation. PET scans were performed for these subjects. During the study, profiles of mood scales were obtained to rate how they were feeling while they were watching the short video presentations. Correlational analyses will be performed to gauge the relationship between behavioral tests and changes in regional glucose metabolism when we have more than 12 subjects in each group.

This project involves human subjects.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$100,000 |

PET Study of Acetaldehyde Distribution and Metabolism to Better Understand Alcohol Related Diseases

Zizhong Li

03-103

PURPOSE:

Modern clinical research has revealed that the harmful effect of ethanol on human health in general is worse than previously expected. Ethanol is different from other drugs of abuse. Ethanol and its metabolites are small and rapidly diffusible molecules and no highly selective binding site has yet been discovered. Conventional pharmacology research methods give little, if any, information about how ethanol and its metabolites interact with the brain and other organs of interest. The objectives of this LDRD project are to synthesize carbon-11 and carbon-11 and deuterium dual labeled ethanol and acetaldehyde with high chemical and radiochemical purity for evaluating the alcohol pharmacokinetics in primates by Positron emission tomography (PET). Upon achieving the objective, we hope to provide a unique research tool to study the biochemical toxicity of ethanol and acetaldehyde in humans and to obtain the information to better understand the biological mechanism of alcohol related disease.

APPROACH:

The chemical route to synthesize the carbon-11 labeled ethanol was developed in the early 1970s. The obstacle for the application of this tracer for dynamic PET studies is its low chemical and radiochemical purity in a form suitable for intravenous injection. Our approach is to develop post-synthesis purification and formulation methods, then

conduct PET studies in primates. Synthesis and PET study of carbon-11 labeled acetaldehyde have not yet been described in literature. Our strategy is to develop a suitable chemical or biochemical method to convert pure [C-11] ethanol into pure [C-11] acetaldehyde and then formulate it into injectable PET tracer suitable for human studies.

TECHNICAL PROGRESS AND RESULTS:

The major technical progress is described as follows: (1) Developed the methodology to synthesize pure injectable C-11 labeled and C-11 and deuterium dual labeled ethanol. (2) Developed methodology to synthesize pure injectable C-11 labeled acetaldehyde. (3) Conducted PET brain scans in primates and established the distribution profile in different brain regions. (4) Measured ethanol uptake and elimination profile in peripheral organs, such as liver, heart, lungs and kidneys in baboons. (5) Measured the brain uptake profile of ethanol after oral administration. The accomplishments of (1) and (2) can be singled out as major technical milestones of this project. The PET results convinced us that we established a new and exciting method for alcoholism research, which can be rapidly translated to humans and enable us to compare alcohol pharmacokinetics in normal controls and in alcoholic patients, and to study other variables, such as gender, "ALDH2 gene knockout models" among different ethnic groups and environmental induced alcohol sensitivity.

In the following fiscal year, we plan to complete the PET studies of the C-11 labeled ethanol and acetaldehyde, publish results, apply for permission to do human studies and use the results obtained from this LDRD research as preliminary data for an application to NIH (National Institutes of

Health) grants to make funds available to continue this research.

The Institutional Animal Care and Use Committee of Brookhaven National Laboratory approved this work. The baboons were housed and maintained in an accredited animal husbandry facility that was approved by the Association for Assessment Laboratory Animal Care.

This project involves animal vertebrates.

SPECIFIC ACCOMPLISHMENTS:

(1) An invited presentation to International Conference On Applications of

Neuroimaging to Alcoholism (ICANA), Yale University, CT, January 17-19, 2004.

(2) Travel Award from ICANA for attending ICANA, Yale University, CT, January 17-19, 2004.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$100,000 |

Hydrogen Atom Transfer from Carbon to Metal — Relevance of a Novel Reaction to Catalyzed Hydrocarbon Conversions

Morris Bullock

03-104

PURPOSE:

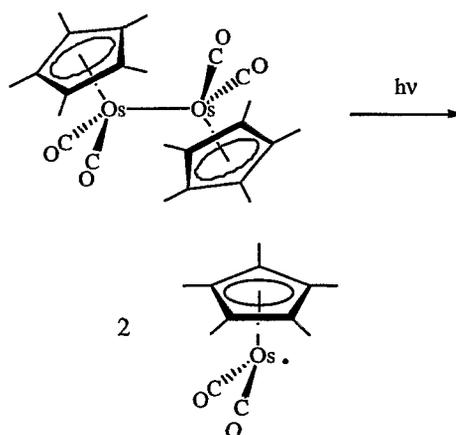
The purpose of this project is to investigate the feasibility of achieving a new method for activation of carbon-hydrogen (C-H) bonds, through hydrogen (H) atom transfer reactions from a carbon to a metal. We seek to carry out fundamental kinetic and mechanistic studies to investigate this novel type of chemical reaction that is relevant to homogeneously catalyzed hydrocarbon conversions.

APPROACH:

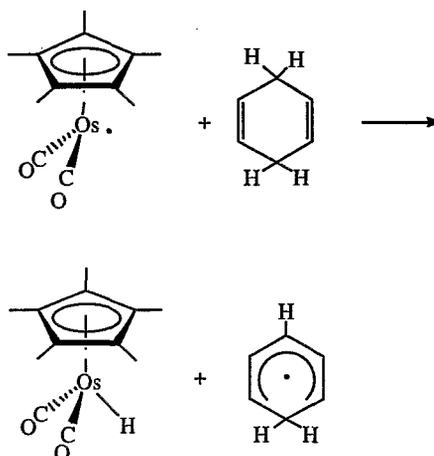
Rational design of new homogeneous catalysts requires a detailed understanding of the individual reactions that collectively constitute a catalytic cycle. Knowledge of the kinetic and thermodynamic parameters for the separate reaction steps can provide an assessment of the viability of such steps operating in catalytic reactions. Thus, fundamental studies of new chemical reactions can lead to the successful incorporation of these reactions into new catalytic cycles. We seek to directly observe a very rare type of reaction, in which a hydrogen atom transfer occurs from a C-H bond to a photochemically generated metal-centered radical. Normally hydrogen atom transfers are favored in the opposite direction, but with a suitably weak C-H bond to cleave and a correspondingly strong metal hydride bond to be formed, the reaction should be feasible. This novel type of reaction could be an important step in the

context of C-H bond activation for hydrocarbon conversions. Selective conversion of hydrocarbons to functionalized organic compounds presents a formidable scientific and practical challenge and remains a major goal of organometallic chemistry and homogeneous catalysis.

The osmium complexes that will be initially examined contain Os-Os bonds that can be photochemically cleaved to generate metal-centered radicals, as shown here.



Hydrocarbons such as 1,4-cyclohexadiene have a weak C-H bond. We seek to measure the rate of the hydrogen atom transfer shown below using a time-resolved transient infrared spectroscopy instrument in the Chemistry Department.



Our recent work in reactions of metal hydrides has focused on cleavage of the M-H bond as a proton (H^+) and as a hydride (H^-), and the use of such reactions in hydrogenations. Homolytic reactivity of M-H bonds can also occur but typically this is used to cleave the M-H bond rather than to form it. It is well-known that osmium forms very strong Os-C and Os-H bonds, so this project seeks to exploit this property to observe and develop the chemistry of hydrogen atom transfers that produce an Os-H bond. On the basis of estimated bond dissociation energies of Os-H bonds, hydrogen atom transfers from carbon to osmium should be thermodynamically feasible under appropriate conditions.

The experiments using transient infrared spectroscopy measurements will be carried out in collaboration with two scientists in the Chemistry Department, Dr. Etsuko Fujita and Dr. David Grills, both of whom have much experience in flash photolysis and transient infrared measurements.

TECHNICAL PROGRESS AND RESULTS:

An extensive international search was conducted to select a postdoctoral research associate with expertise in the ability to synthesize and manipulate exceedingly air-sensitive organometallic materials, as well as expertise in mechanistic experiments and

other physical measurements of such complexes. Dr. Jie Zhang recently worked with Prof. Poliakoff and Prof. George at the University of Nottingham (U.K.) and accepted an offer from BNL. His arrival at BNL has been severely delayed since we have been waiting for approval of his visa. This has caused substantial frustration and has impeded progress.

Initial efforts will involve significant synthetic experiments to prepare the osmium complexes to be studied. One problem that has thwarted extensive development of the chemistry of some types of osmium complexes is a paucity of attractive, high-yield routes to prepare them, so our expertise in synthetic organometallic chemistry will assist this effort. The second phase will involve exploration of the photochemistry of the complexes, as a prelude to the use of the time-resolved step-scan infrared spectrometer for the hydrogen atom transfers.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$30,000 |
| FY 2004 (budgeted) | \$80,000 |

Radioprotection in *D. Radiodurans*, a Radiation Resistant Bacterium

Diane Cabelli

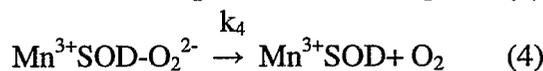
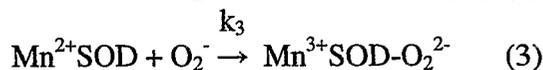
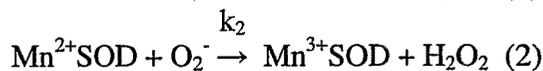
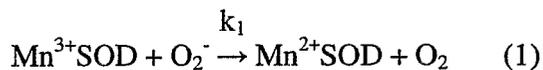
03-105

PURPOSE:

Deinococcus radiodurans (*Dr*) is an extremely radiation resistant bacterium where the resistance drops significantly when the manganese superoxide dismutase (MnSOD, metalloenzyme that dismutates superoxide (O_2^-) to O_2 and H_2O_2) is cloned out of the organism. The use of bacteria for the remediation of heavy metal and radioactive waste (e.g. isotopes of uranium and plutonium, mercury) is very promising, and efforts to engineer remediation function into *Dr* or to enhance the bacterium's existing ability to reduce heavy metals is underway elsewhere. We are proposing to study the MnSOD in *Dr* to determine whether enzymatic activity has been optimized in the evolution of this radiation resistance. We also propose to study the effects of radiation and free radicals on membrane components and surface structure of *Dr*. Understanding the basic differences between *Dr* and other organisms in the above-mentioned systems (MnSODs, membrane components, membrane surface) may allow us to engineer radiation resistance into other bacterial systems that are already useful in non-radioactive cleanup.

APPROACH:

MnSOD eliminates superoxide through the mechanism shown below, where the reduced enzyme can react with superoxide through an outer or inner sphere reaction (2 or 3). The gating between the rates of these two-steps will determine the efficiency of the enzyme, depending on O_2^- concentration.



In order to understand an aspect of the extreme radioresistance of *Dr*, we will measure the various reactions in the mechanism described above using the fast kinetic technique of pulse radiolysis found at BNL. We will compare the reactivity of *Dr* MnSOD with that of *E coli* MnSOD and human MnSOD. The crystal structure of the *Dr*MnSOD can also be compared with those of *E coli* and human MnSODs in order of function to structure.

We will also use the radiation chemistry facility at BNL to address reactivity of membrane components (e.g., aconitase, catalase). A longer-term goal is to look at membrane surface structure of *D radiodurans* both before and after irradiation to help understand radiation resistance and surface membrane changes.

Postdoctoral Research Associate: Dr. Isabel Abreu arrived on January 15, 2003, to begin work on this project.

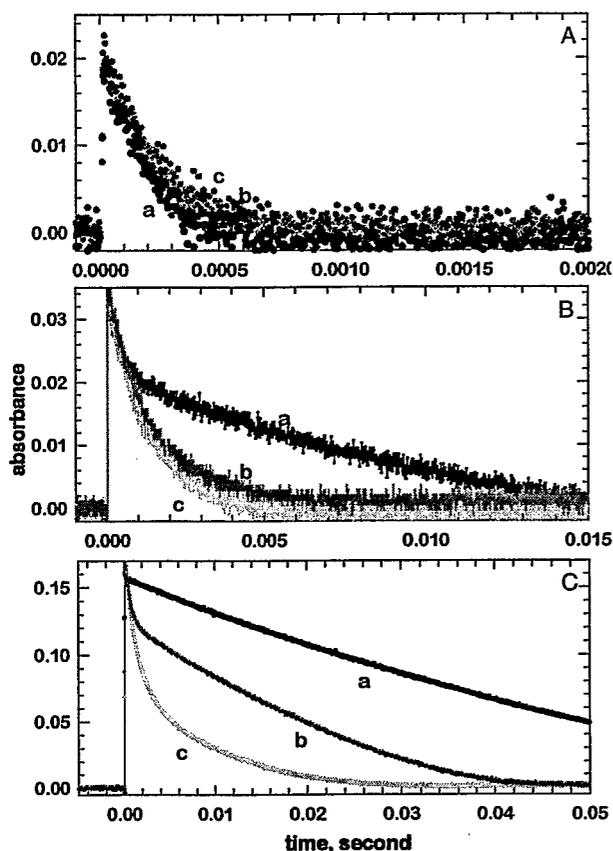
Collaborators: Professor David Silverman, University of Florida for the expression, isolation and purification of MnSOD from *D. radiodurans*.

Professor Geoff Jameson, University of New Zealand for determination of the crystal structure of the MnSOD.

TECHNICAL PROGRESS AND RESULTS:

Using pulse radiolysis, we followed the disappearance of varying concentrations of superoxide radical in the presence of *Dr*, *E*

coli and human MnSODs on the microsecond and millisecond time scale.



In panel A, the concentrations of O₂^{·-} and MnSOD are equal (5 μM). Under these conditions, O₂^{·-} disappears at equally fast rates for all of the enzymes; hMnSOD, *E. coli* MnSOD and *DrMnSOD*. In equimolar concentrations, only k₁ or k₂ are accessed and the rate constants are identical.

Under catalytic conditions, however, where the ratio of O₂^{·-} to MnSOD is 7:1 (panel B), the human enzyme is already noticeably less efficient at removing superoxide. In the human MnSOD, the O₂^{·-} is partitioning equally between formation of an inactive complex and an outer sphere mechanism, and release of the bound peroxide (k₄) becomes rate limiting.

In the presence of 43 μM superoxide and 1 μM MnSOD (Panel C), the *E. coli* and the *Dr*

MnSODs also react by partitioning between formation of an inactive complex and an outer sphere mechanism. The dramatic difference observed here is that within 3 millisecc, over half the superoxide has disappeared in the presence of *DrMnSOD*, while less than 25% has disappeared in the present of *E. coli* MnSOD and only a few percent has disappeared in the presence of hMnSOD. This so far unique characteristic of *DrMnSOD* will be physiologically relevant in an organism such as *Dr*, since the high levels of radiation it endures will have as primordial effect the enhancement of intracellular ROS. This enhanced activity helps explain the role *DrMnSOD* plays in radioresistance and why *Dr* cells lacking the enzyme are more susceptible to radiation damage.

Our future plans are to continue characterizing *DrMnSOD* with regards to thermal stability and pH. The crystal structure has been determined to low resolution and data is being refined to greater resolution. In addition, we are planning to try cloning *DrMnSOD* into *E. coli* and to look at radiation resistance in the modified *E. coli*. Finally, we would like to begin looking at surface structure of the enzyme with and without radiation exposure.

SPECIFIC ACCOMPLISHMENTS:

I. A. Abreu, H. An, A. S. Hearn, H. Nick, D. N. Silverman and D. E. Cabelli. *Deinococcus radiodurans* manganese-containing Superoxide Dismutase as a Specialized enzyme for the elimination of high superoxide concentrations, to be submitted.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$57,500 |
| FY 2004 (budgeted) | \$75,000 |

New Development of Norepinephrine Transporter Radioligands for PET Studies of Substance Abuse, Depression and ADHD

Yu-Shin Ding

03-107

PURPOSE:

Research on dopamine (DA) and serotonin (SER) systems related to various Central Nervous System (CNS) disorders has benefited from the availability of suitable radioligands. The norepinephrine transporter (NET) has long been recognized in relation to the pathophysiology and treatment of Attention Deficit Hyperactivity Disorder (ADHD), substance abuse and depressive disorders. However, brain imaging of NET has been hampered by the lack of suitable radioligands. The fact that all three transporters (NET, dopamine (DAT), and serotonin (SERT)) are involved in various neurological and psychiatric diseases places a sense of urgency to develop new NET ligands so that we will be able to tease out the roles of individual transporters underlying specific CNS disorders.

APPROACH:

Reboxetine, (RS)-2-[(RS)- α -(2-ethoxyphenoxy)-benzyl]morpholine (RB), is a specific NET inhibitor with a high affinity and high selectivity (IC_{50} DAT/NET = 4000), and it has been approved for the treatment of depressive illness in several European countries. The purpose of this project is to synthesize and evaluate a C-11 labeled analogue of reboxetine ($[^{11}C]$ O-methyl-reboxetine, ($[^{11}C]$ MRB) for PET imaging studies of NET in non-human primates.

TECHNICAL PROGRESS AND RESULTS:

Materials and Methods

Synthesis of precursors and radiosynthesis of $[^{11}C]$ MRB, (R,R)- $[^{11}C]$ MRB and (S,S)- $[^{11}C]$ MRB

The normethyl precursor was synthesized via a multi-step regio- and stereospecific synthesis starting from a mono-O-protected catechol. The resulting racemic mixture of normethylreboxetine was resolved by chiral HPLC to provide (2S;3S) and (2R;3R) enantiomers with > 98% enantiomeric excess. These compounds were then used as precursors for radiosynthesis to prepare enantiomerically pure individual C-11 labeled MRB for comparative PET studies in baboon.

Comparative PET Studies in Baboon Brain and Torso: PET Studies of $[^{11}C]$ MRB, (R,R)- $[^{11}C]$ MRB and (S,S)- $[^{11}C]$ MRB were carried out in three adult female baboons (*Papio anubis*), which were prepared for PET studies as described previously (Ding, et al., 1995).

Drug Administration: The pharmacological profiles of $[^{11}C]$ MRB, (R,R)- $[^{11}C]$ MRB and (S,S)- $[^{11}C]$ MRB binding in baboon brain were determined by carrying out a baseline PET study and then pretreating with an intravenous injection of nisoxetine (0.5-1.0 mg/kg), a selective NET blocker, prior to the second injection of $[^{11}C]$ MRB, (R,R)- $[^{11}C]$ MRB or (S,S)- $[^{11}C]$ MRB. Blocking studies in periphery with desipramine (0.5 mg/kg, 40 min prior to the tracer injection), a selective NET inhibitor, were performed to determine whether NET blockade affected the uptake and kinetics of (R,R)- $[^{11}C]$ MRB or (S,S)- $[^{11}C]$ MRB in the NET rich organs, such as the heart. The dose and pretreatment time of desipramine used for these studies was based on our previous studies of F-18 labeled catecholamines in the heart (Ding, et al., 1993, Ding, et al., 1995).

Plasma Analysis: Two methods (A: HPLC method; B: robotic solid phase extraction) were employed to determine the percentage of unchanged labeled radiotracers in plasma.

Region of interest (ROI) selection: Methodologies for brain and torso image analysis (Ding, et al., 1997, Ding, et al., 2000) and torso image analysis (Ding, et al., 1998, Ding, et al., 1993) have been described previously.

Data analysis: Time-activity curves in various regions were expressed as %injected dose/cc (decay corrected) in specific ROI with time. Time-activity curves for carbon-11 and the time course of unchanged tracer in plasma were used to calculate distribution volume (DV) in regions of interest using a graphical analysis method for reversible systems (Logan plots) as previously described (Logan, et al., 1990).

Results

Baseline studies of the racemic compound (^{11}C]MRB) in baboons showed a moderate brain uptake (0.01-0.02 %injected dose/cc) and the distribution of carbon-11 was heterogeneous with the highest uptake and slow washout (half-time for clearance was approximately 110 min) occurring in the thalamus, a known NET-rich region. A test-retest study in the same baboon indicated a good reproducibility of the tracer binding (within 8%). The radiotracer uptakes in the thalamus and cerebellum (NET rich regions), but not in the striatum (NET poor region), were significantly reduced by the pretreatment with nisoxetine (0.5 mg/kg, 30 min prior to tracer injection). However, no blocking effect on the uptakes of ^{11}C]MRB was observed when baboons were pretreated with GBR12909 (data not shown). These results indicated the specific binding of the tracer to NET. Comparative studies of the individual enantiomers ((R,R)- ^{11}C]MRB and (S,S)- ^{11}C]MRB) in the same baboon were then carried out. Their half-times for clearance from peak uptake in thalamus were dramatically different; they were approx. 95 and 250 minutes for (R,R)- ^{11}C]MRB and (S,S)- ^{11}C]MRB, respectively. With (S,S)- ^{11}C]MRB, there was a slow clearance of radioactivity in NET rich regions such as the thalamus and cerebellum and a faster washout in the striatum and cortical regions. In contrast, (R,R)- ^{11}C]MRB displayed similar uptakes with similar half-times for clearance for all the regions. Though there was inter-subject variability in the absolute DV values, as indicated by standard deviations, a significantly higher (2 fold) thalamic DV for (S,S)- ^{11}C]MRB was observed as compared to ^{11}C]MRB or (R,R)- ^{11}C]MRB.

Pretreatment with nisoxetine (1.0 mg/kg) 10 min prior to (S,S)- ^{11}C]MRB injection markedly reduced the uptakes in the thalamus (~50%) and cerebellum (~40%), but not that in the striatum, demonstrating the saturable and specific binding of (S,S)- ^{11}C]MRB to the NET in the brain. In contrast, nisoxetine had no significant effect (within the standard deviation) on the binding of (R,R)- ^{11}C]MRB.

In the baboon torso, uptakes in most of the peripheral organs were generally higher for (S,S)- ^{11}C]MRB than for (R,R)- ^{11}C]MRB. Pretreatment with desipramine resulted in a reduced heart uptake as compared to that of the baseline after injections of (S,S)- ^{11}C]MRB. This reduction of uptake after desipramine was only observed in the heart and no significant changes were observed in the uptakes of the lung or liver. A slightly increased uptake in the kidneys after desipramine was perhaps due to, in part, an increased excretion process. In contrast, at the end of the study (90 min) after injection of (R,R)- ^{11}C]MRB there was no significant reduction in the heart uptake after desipramine. These results further demonstrated the specific binding of (S,S)- ^{11}C]MRB for NET in both brain and whole body.

The results of the assays for unchanged tracer in baboon plasma via the HPLC and solid phase extraction methods gave similar results. Metabolism of (S,S)- ^{11}C]MRB and (R,R)- ^{11}C]MRB were compared after *i.v.* injection of individual enantiomers in the same baboon. Assays of the fraction of unchanged (S,S)- ^{11}C]MRB and (R,R)- ^{11}C]MRB in plasma afforded similar results with 98%, 59%, 41%, 30%, 26% for (S,S)- ^{11}C]MRB, and 98%, 54%, 44%, 39%, 33% for (R,R)- ^{11}C]MRB at 1, 5, 10, 30, 60 min, respectively. Only polar metabolites were found in baboon plasma following *i.v.* injection of individual enantiomers.

Discussion

Our studies in baboons after intravenous injections of (R,R)- ^{11}C]MRB and (S,S)- ^{11}C]MRB demonstrate a slightly higher, though not significantly higher, plasma concentration

for the inactive enantiomer of methyl analogue of reboxetine, i.e. (R,R)-[¹¹C]MRB, as compared to (S,S)-[¹¹C]MRB.

All three radiotracers displayed unexpected high uptakes in striatum, a region that is supposed to contain low levels of NET. However, these uptakes represent only non-specific binding, which was demonstrated by the blocking studies with a specific NET inhibitor, nisoxetine. That is, there were no significant changes in the striatal uptakes with and without the nisoxetine pretreatment. In contrast, a significant blocking effect was observed in NET rich regions such as thalamus and cerebellum after injection of racemic [¹¹C]MRB, with an even greater blocking effect after injection of (S,S)-[¹¹C]MRB. These results, along with the fact that no regional specificity and no blocking effect by nisoxetine were observed for (R,R)-[¹¹C]MRB, suggest the enantioselectivity of MRB in vivo, which is consistent with previous in vitro and in vivo studies in rodents (Wilson, et al., 2003, Wong, et al., 2000). The possibility for the existence of low affinity binding sites in striatum to account for the high striatal uptake has not been ruled out. In fact, this has been shown in previous studies in NET and other neurotransmitter systems (Yavin, et al., 1978, Biegon et al., 1979). Further investigations are required.

(-)-Norepinephrine is the principal neurotransmitter of the sympathetic nervous system. Drugs which affect the NET in the brain may also affect the NET in the heart and thus the development of specific radioligands for the NET has the potential to assess the effects (and potential side effects) of NET-specific drugs on the heart. Cocaine, for example, has been shown to have an effect on the NET in the heart, which is of longer duration than the presence of cocaine (Fowler, et al., 1994). The present study to characterize the specific binding of [¹¹C]MRB to the NET systems both in brain and periphery also indicated a stereoselective inhibition by desipramine on the uptake of (S,S)-[¹¹C]MRB, but not that of (R,R)-[¹¹C]MRB, in the heart.

This strategy of studying NET in brain with PET is a new direction that complements many of our longstanding interests in studying substance abuse and ADHD (Ding, et al., 1997, Ding, et al., 1994, Fowler, et al., 1999, Volkow, et al., 1998, Volkow, et al., 1995, Volkow, et al., 2001, Volkow, et al., 2002). Based on the recent studies in rat brain and our present studies in baboon brain, the active enantiomer of this C-11 labeled methyl analogue of reboxetine, (S,S)-[¹¹C]MRB, has demonstrated encouraging in vivo specificity and selectivity as a potential NET ligand for studying the NET system with PET. The mechanism for a relatively high uptake, though only representing the non-specific binding in the striatum, is not known. However, to our knowledge, (S,S)-[¹¹C]MRB is by far the most promising in vivo NET radiotracer with adequate pharmacokinetic and metabolism, and is expected to provide specific and functional maps of NET in the brain. These studies will allow a better understanding of the role that NET plays in living systems, and they set the stage for drug development and future examination of ADHD, substance abuse, depression and anxiety disorders. Since the pharmaceutical industry is involved in the development of NET inhibitors for the treatment of ADHD, depression and mood disorders, and as some of these are undergoing clinical investigation, we envision that the use of (S,S)-[¹¹C]MRB with PET will provide the opportunity to directly assess the pharmacodynamics of these drugs in the human body. Furthermore, the ability to map NET in vivo will provide the first opportunity to track its role in vivo. It will also be an important tool in preclinical studies in transgenic animals particularly monoamine knockouts using MicroPET. Because of the importance of the monoamine neurotransmitters and their association with motor activity, cognition and mood, this will be an important advance.

Summary

Reboxetine is a specific norepinephrine transporter (NET) inhibitor and has been marketed in several countries as a racemic mixture of the (R,R) and (S,S) enantiomers for the treatment of depression. Its methyl analogue

(methylreboxetine, MRB) has been shown to be more potent than reboxetine itself. We have developed a nine-step synthetic procedure to prepare the normethyl precursor, which was used to synthesize [¹¹C]O-methylreboxetine ([¹¹C]MRB). We have also developed a convenient resolution method using a chiral HPLC column to resolve the racemic precursor to obtain enantiomerically pure individual precursors that lead to the individual enantiomers (R,R)-[¹¹C]MRB and (S,S)-[¹¹C]MRB. Here we report an evaluation of the racemate and individual enantiomers of [¹¹C]MRB as radioligands for PET imaging studies of NET systems in baboons both in brain and in peripheral organs. Our results demonstrated the enantioselectivity of MRB and the specificity of (S,S)-[¹¹C]MRB both in brain and peripheral organs. These studies demonstrate that the use of (S,S)-[¹¹C]MRB would allow a better understanding of the role that NET plays in living systems.

Future Plan

In the coming year (2004), our plans are:

1. Develop and characterize more NET ligands in baboons to search for the most suitable NET tracer with optimal specificity, selectivity and pharmacokinetics for PET studies in humans.
2. Obtain approvals from the FDA and our IRB to carry out studies in humans. This will require a toxicology study of the drug.

In the future, we will try to obtain funding from NIH to carry out human studies to tease out the roles of individual transporters (NET, DAT, SERT) underlying specific CNS disorders. Our ability to map NET in vivo will provide the opportunity to better understand its role in the treatment of ADHD, depression, mood disorders and Alzheimer's disease.

This project involves animal vertebrates.

SPECIFIC ACCOMPLISHMENTS:

Lin, K. S.; Ding, Y.-S. "Synthesis and Evaluation of a New Norepinephrine Transporter PET Ligand in Non-Human Primates," 15th International Symposium on Radio-pharmaceutical Chemistry, Sydney, Australia, August 9-14, 2003.

Ding, Y.-S. "Synthesis and Evaluation of a New Norepinephrine Transporter PET Ligand in Non-Human Primates," Frontiers in Neuroimaging at Department of Energy National Laboratories, Boston, Massachusetts, October 27-29, 2003.

Ding, Y.-S.; Lin, K.-S.; Garza, V.; Carter, P.; Alexoff, D.; Logan, J.; Shea, C.; Xu, Y.; and King, P. "Evaluation of a New Norepinephrine Transporter PET Ligand in Baboons, Both in Brain and Peripheral Organ." Synapse, 50:345-352 (2003).

Lin, K.-S. and Ding, Y.-S. "Synthesis, Enantiomeric Resolution and Selective C-11 Methylation of a Highly Selective Radioligand for Imaging the Norepinephrine Transporter with Positron Emission Tomography." Chirality (submitted).

Ding, Y.-S.; Lin, K.-S. "Development of New Norepinephrine Transporter PET Radioligands in Non-Human Primates," The German annual meeting of the Nuclear Medicine Society, Rostock, Germany, April 2004.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$112,000 |
| FY 2004 (budgeted) | \$112,000 |

Experiments in the Short-Wavelength Regime Pertinent to the DUV-FEL Concept

Louis F. DiMauro

03-108

A. G. Suits

M. G. White

PURPOSE:

In this proposal, we outline the development of the first experimental end-station at the DUV-FEL (deep ultraviolet free-electron laser) and the first experiments to take advantage of this unique light source. The proposed experiments represent groundbreaking work in the short-wavelength regime in chemical physics, photodissociation, reaction dynamics and atomic and molecular (AMO) physics, yet benefit from the rich history of intense light-matter interaction done with traditional light sources at longer wavelengths. The experiments initially concentrate on imaging ion pair dissociation dynamics, photoelectron imaging, pump-probe photodissociation dynamics, surface dynamics and non-linear ionization of rare gases, where the simultaneous absorption of two or more photons liberates a bound electron.

APPROACH:

BNL has been a leader in the development of accelerator-based light sources that have opened fundamental new areas of scientific endeavor. The most recent project in this regard is, the Deep Ultraviolet Free Electron Laser (DUV-FEL) at the Source Development Laboratory (SDL), which is a short wavelength, high intensity source based on the principle of seeded, high-gain, high-harmonic (HGHG) single-pass amplification. The HGHG approach is unique to BNL and offers a FEL source with

fully coherent short wavelength output and superior stability as compared to alternate schemes, e.g. SASE (Self Amplified Spontaneous Emission).

The need for a cutting-edge scientific program to take advantage of this novel light source is clear. The present co-investigators describe a multifaceted scientific program in chemical dynamics, atomic physics and surface dynamics that all rely on a single, versatile endstation. The proposed experimental objectives adapt to and benefit from the evolution of the DUV-FEL output towards shorter wavelength. Once these experiments are successfully demonstrated, we anticipate ongoing support for these studies from the BES (Basic Energy Sciences) Fundamental Interactions program.

TECHNICAL PROGRESS AND RESULTS:

The endstation, shown in Figure 1, was assembled and detected the first XUV photons from the DUV-FEL in December 2002. The first series of ion pair imaging studies began in January 2003 and a rich system suitable for investigation at the wavelength of the FEL third harmonic, i.e. 89nm, was identified in methyl fluoride. The detailed dynamics of ion pair dissociation in this system were revealed through measurements of the F⁻ ion images and in supporting theoretical work by R. Lucchese at Texas A&M.

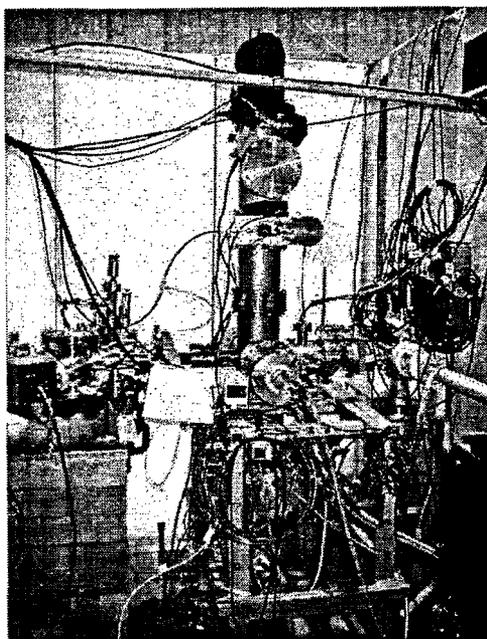


Figure 1. Imaging endstation at the DUV-FEL

Milestones for FY 2004 include investigation of photoelectron imaging in oxygen, in which autoionizing superexcited state contributions to photoabsorption are believed to be important. Additional new directions with this source include universal imaging of photodissociation dynamics.

SPECIFIC ACCOMPLISHMENTS:

This work was presented in posters at a symposium on "VUV probes of spectroscopy and dynamics" at the 225th national ACS (American Chemical Society) meeting in March 2003 and at the Waterloo Chemical Physics symposium in November 2003. In addition, it was featured in oral presentations to the Gordon Conference on "Electronic Spectroscopy and Dynamics" at Bates College in July, 2003, at the COMET meeting in San Lorenzo de El Escorial, Spain, in July 2003 and to a joint Chemical Dynamics Beamline/AMO Physics Beamline seminar at the Advanced Light Source in Berkeley in August. It was presented at a review of the PI's core program in Chemistry recently and it formed the focus of discussions in a workshop on scientific directions for the DUV-FEL, jointly organized by the PI and the Director of the Light Source.

A joint proposal between Chemistry and the SDL is likely to be developed in the coming months, to be directed to DOE.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$132,000 |
| FY 2004 (budgeted) | \$132,000 |

Imaging Tandem Mass Spectrometry for High-Throughput "Fingerprint" Detection of Complex Molecules in Mixtures

Arthur G. Suits
G. E. Hall

03-115

PURPOSE:

We propose to develop an *imaging approach to tandem mass spectrometry*. In this approach, the single-shot, multiplexing data acquisition is matched to the data structure, allowing both improved efficiency and throughput, but also making apparent parent-daughter ion correlations and metastable decay mechanisms. These, in turn, will reveal distinct signals and decay dynamics for particular molecules, allowing sensitive detection and unique markers for complex molecules in mixtures. The results will have broad possible applications in proteomics, ultimately leading to possible support through DOE (Department of Energy), NIH (National Institutes of Health) and other agencies.

APPROACH:

Mass Spectrometry is revolutionizing the study of complex molecules and anticipated advances in proteomics now hinge upon the central contributions of mass spectrometric methods. All of these approaches exploit the advantages of tandem mass spectrometry, in which a particular product mass is chosen out of a sample, then submitted to some chemical or physical interaction, after which a second mass spectrum is recorded. Particular challenges for both counter-terrorism applications and those in proteomics include: the ability to characterize a specific complex molecule in

a mixture, the need for high-throughput screening strategies that do not sacrifice accuracy (both high sensitivity and no false positives) and the ability to incorporate a variety of secondary interactions in the tandem mass spectrometer to develop appropriate sensitive probes for the species of interest. We propose to develop an alternative approach to tandem mass spectrometry that relies upon recent advances in ion imaging techniques promising advantages in throughput and sensitivity compared to traditional approaches.

Tandem mass spectrometry is inherently a multidimensional technique, yet *all current applications rely on one-dimensional data recording*. This surprising state of affairs leaves us with approaches that are not only inherently less efficient; as a parent mass must be selected, a fragment mass spectrum recorded, then the process repeated, but it further sacrifices potential correlations between parent and daughter ions that can provide additional insight and may represent unique markers for specific molecules. Imaging methods have recently emerged as a powerful means of achieving simultaneous detection of the complete product velocity distribution for ions of a given mass, and these approaches have recently been extended to multimass detection strategies. We propose coupling velocity map imaging with tandem mass spectrometry to achieve an imaging tandem mass spectrometry (iMSⁿ). This promises to yield a high-throughput, "fingerprint" mass spectrometry, wherein the data acquisition itself is well-matched to the data structure and overlooked correlations may be revealed and exploited to improve sensitivity and accuracy. Images resulting from this approach will embody the complete tandem mass spectrum recorded in a single shot.

TECHNICAL PROGRESS AND RESULTS:

In the first half of FY 2003, extensive ion trajectory simulations were performed in order to identify the optimum strategy for pursuing imaging mass spectrometry. The trajectory simulations demonstrated the feasibility of achieving velocity map focusing in a "reflectron" mode. Furthermore, the simulations showed that short pulse deflection is capable of a tunable, spatially resolved mass dispersion. This was the key to developing the final instrument design. A post-doc was hired in mid-year to join the student on the project and construction of the apparatus began in earnest. All of the components have been fabricated and assembled, as shown in Figure 1.

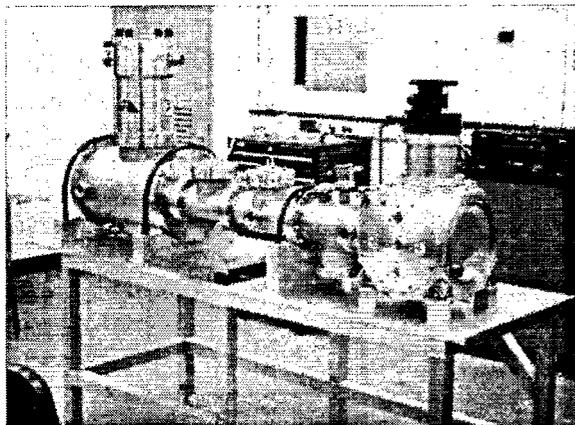


Figure 1. - Photograph of imaging tandem mass spectrometry apparatus undergoing assembly.

The milestones for the project in FY 2004 include: the first demonstration of velocity map focusing in a reflectron configuration, spatially resolved mass discrimination using pulsed electric fields and finally, imaging tandem mass spectrometry. This will lead directly to applications in proteomics.

SPECIFIC ACCOMPLISHMENTS:

In mid-year, funding (total \$40K) was obtained through Stony Brook University jointly from the New York Center for Biotechnology and the Sensor Center for Advanced Technology.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$113,000 |
| FY 2004 (budgeted) | \$113,000 |

Condition: Green Chemistry.

Radiolytic Studies of Ionic Liquids in Service of Security and the Environment

James Wishart

03-118

PURPOSE:

The objective of this project is to understand the radiation chemistry of ionic liquids (low-melting salts), a new class of solvents that can be safer and more environmentally benign alternatives to present technology. Radiolysis studies are needed to determine the radiation stability of ionic liquids for applications as media for nuclear fuel processing and for developing methods to study chemical kinetics in these novel solvents. The time resolution of BNL's LEAF (Laser-Electron Accelerator Facility) facility is uniquely suited to this work. Results of this study may lead to new, ionic liquid-based initiatives in photochemical energy storage, including (H₂ and methanol production), nanoscience, chemistry related to actinide processing and a large, multi-investigator, multi-institution project to study the physical chemistry of ionic liquids.

APPROACH:

Ionic liquids have broad applications as media for chemical transformations and in the study of chemical reaction mechanisms. Pulse radiolysis is an important and in some ways unique method of studying chemical kinetics. In order to use pulse radiolysis to study reactions in ionic liquids, the yields and chemistry of the primary radiolysis products must be known. Our approach is to use BNL's Laser-Electron Accelerator Facility to identify reactive species and measure their reaction rates. In the later phase of this project, we will use our findings to study charge transport and other reactions that are

relevant to chemical conversion of solar energy.

The physical properties of ionic liquids can be varied over an extremely wide range, with dramatic effects on reactivity. We design and prepare ionic liquids with desired properties in our lab and through collaborations with Prof. Robert Engel of Queens College, CUNY. We characterize the physical properties of our liquids by several techniques including AC conductivity and viscometry. Solvation dynamics is a very important facet of reactivity in ionic liquids. We collaborate with Prof. Edward Castner of Rutgers to measure the solvation response of our ionic liquids using time-resolved emission spectroscopy of solvatochromic dyes and with Prof. Mark Kobrak of Brooklyn College, CUNY on molecular dynamics simulations of solvation phenomena.

"Criticality safe" ionic liquids (containing high concentrations of thermal neutron scavengers boron and/or chlorine) with good fluid properties would be useful as safer alternatives for nuclear processing applications. It is important to find out what kinds of radiolysis products are formed in these liquids and how can the liquids be made radiation-stable. We have established a collaboration with Prof. Christopher Reed of U. C. Riverside to design ionic liquids containing inert carborane anions and study their radiation chemistry.

Four undergraduate summer research interns and one summer visiting professor were sponsored through three educational programs to participate in this project.

TECHNICAL PROGRESS AND RESULTS:

We have measured solvated electron spectra in all of our liquids in which it was observed. The spectra fall into classes differentiated by the shape of the ionic liquid cation. This provocative result implies that the energetics

of reactive species in ionic liquids can be controlled through very subtle modification of the liquids.

Our results have shown that the reactivity of pre-solvated electrons is a much more significant aspect of the overall chemistry in ionic liquids than in conventional solvents. We have found that electron solvation occurs 1000 times slower in some ionic liquids in molecular solvents. We have confirmed the slow solvation dynamics using laser flash photolysis of solvatochromic dyes.

Novel ionic liquids with lower melting points and viscosities were developed. Some of them flow so easily that it becomes possible to observe pre-solvated electron decay directly using NIR pulse-probe at LEAF, once the appropriate NIR detectors are installed.

A new family of proton-donating ionic liquids ($R_3NH^+NTf_2^-$) was developed as a medium to study H-atom reactions in the absence of (previously required) water. This cleaner system for H-atom studies enables the study of pre-solvated electron capture without complications from solvated electrons (which react immediately with R_3NH^+).

Synthetic work on carborane ionic liquids provided a couple of examples of low-melting solids whose radiation chemistry is currently under study. Preliminary results indicate that the liquids are reasonably inert, with radical-radical recombination being the major decay process of the transient species.

We have determined the temperature dependence of the viscosities and conductivities of our liquids to learn more about how to control their properties. We have measured solvated electron reaction rates with O_2 and CO_2 in several liquids. These and earlier H-atom reaction rate data indicate that diffusion processes in ionic liquids depend on charge and size in complex ways that could be employed to control reactivity and transport

phenomena when properly understood.

Direct observation of the electron solvation process using NIR pulse-probe is a goal for the next period. Solvation dynamics over a wide range of viscosities will be measured by photolysis. Yields, spectroscopy and reactivity of primary species will be determined for additional classes of ionic liquids. The reactivity of carborane cations dissolved in other types of ionic liquids where the radiation chemistry is already characterized will be examined. Self-diffusion rates of ionic liquid components and solutes will be measured with an NMR (nuclear magnetic resonance) technique to elucidate the non-classical transport behavior in ionic liquids. Studies will begin on the effects of ionic liquids on charge-transport reactions related to solar energy photoconversion.

SPECIFIC ACCOMPLISHMENTS:

Effect of Ether Functionalities on Ionic Liquid Properties. Funston, A. M.; Trofimovsky, E.; Odynecki, K.; Kobrak, M. N.; and Wishart, J. F. Chem. Comm., submitted.

Talks

Radiation Chemistry Studies of "Green" Solvents at BNL's Laser-Electron Accelerator Facility. Symposium on "Research Activities of the New Radiation Laboratory of the Nanoscience and Nanotechnology Center," Osaka University, Osaka, Japan, March 14, 2003.

Radiation Chemistry Studies of "Green" Solvents at BNL's Laser-Electron Accelerator Facility. University of Tokyo Nuclear Engineering Research Laboratory, Tokaimura, Japan, March 17, 2003.

Reactivity of Solvated and Pre-solvated Electrons in Alkylammonium Bistriflylimide Ionic Liquids. Funston, A. M.; Wishart, J. F.; Neta, P.; Brenneke, J. F. 226th ACS National

Meeting, New York, NY, September 7 – 11, 2003.

Radiolysis of Ionic Liquids. Funston, A. M.; Wishart, J. F. Monash University, Melbourne, Australia, August 27, 2003.

Capabilities and Applications of Brookhaven's Picosecond Laser-Electron Accelerator Facility. Funston, A. M.; Wishart, J. F.; Miller, J. R.; Cook, A. R.; Holroyd, R. A.; Poliakov, P.; Takeda, N. 12th International Congress of Radiation Research, Canberra, Australia, August 17 – 22, 2003.

Spectra and Reactivity of Solvated and Pre-solvated Electrons in Ionic Liquids. 23rd Miller Conference on Radiation Chemistry, Bialowieza, Poland, September 11, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity. Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany, September 16, 2003.

Ionic Liquids: Salt *for* the Future. Wishart, J. F. 387th Brookhaven Lecture, BNL, October 15, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity. University of California at Los Angeles, October 29, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity. University of California at Riverside, November 3, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity. University of California at San Diego, November 5, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity.

California State University at Long Beach, November 7, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity. California Institute of Technology, Pasadena, CA, November 10, 2003.

Physical Studies of Ionic Liquids: Properties, Solvation Dynamics and Electron Reactivity. University of California at Santa Barbara, November 12, 2003.

Posters

Ionic Liquids: Composition Effects on Reactivity Patterns and Solvation Dynamics. Funston, A. M.; Wishart, J. F.; Neta, P. 226th ACS National Meeting, New York, NY, September 7 – 11, 2003.

Picosecond Radiolysis of Ionic Liquids. Funston, A. M.; Wishart, J. F.; Neta, P. 12th International Congress of Radiation Research, Canberra, Australia, August 17 – 22, 2003.

Synthesis and Radiolysis of Tertiary Alkyl Ammonium Bis(trifluoromethanesulfonyl)imide Ionic Liquids. Ramkirath, R. D. BNL Summer Undergraduate Internship Programs Poster Session, August 7, 2003.

Synthesis and Characterization of Pyrrolidinium Ionic Liquids. Trofimovsky, E. BNL Summer Undergraduate Internship Programs Poster Session, August 7, 2003.

With collaborators on several CUNY campuses, we have requested student support from the Alliance for Minority Participation. Opportunities for joint proposals with Kobrak and Castner are being explored.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$43,000 |
| FY 2004 (budgeted) | \$80,000 |

Exploring the Use of Powder Diffraction for Proteins

Marc Allaire

03-119

PURPOSE:

Over the last decade structural biology revolutionized the drug discovery process. A major development would be in the screening of a specific protein with a library of chemicals to identify lead compounds and at the same time generate three-dimensional structure information on the binding modes of the target. Protein powder diffraction represents an attractive alternative for High-Throughput Screening of protein/ligand complexes. A major drawback is on the limited resolution of the macromolecular structure determined from powder data. The purpose of this study is to verify if protein powder diffraction can be used for screening chemicals and is sufficient to describe the binding modes of a targeted macromolecule.

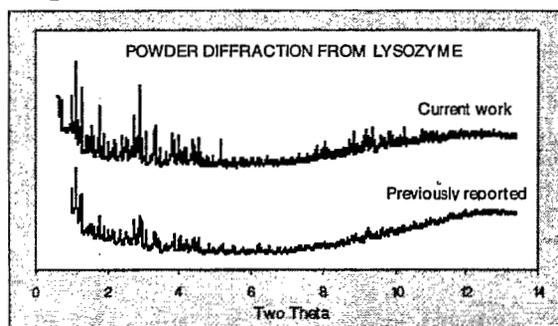
APPROACH:

Recent works (Von Dreele et al. (2000) *Acta Cryst.*D56,1549-53; Von Dreele (2001) *Acta Cryst.*D57,1836-42) done on insulin and lysozyme reveal that powder diffraction data can be used for structure determination. The work done on lysozyme and lysozyme bound to N-acetylglucosamine, suggests the potential of powder diffraction to locate ligands but also reveals the poor quality of electron density map to identify clearly the chemical complex in the protein.

For screening, we may expect that powder diffraction data of bound and unbound lysozyme should be different. In order to identify the binding modes of the protein, we need to improve the electron density image of the ligand bound to the protein. A simple approach is to improve the quality of the powder produced from the protein.

TECHNICAL PROGRESS AND RESULTS:

Obtaining better powders produced from lysozyme was explored using different concentrations of lysozyme and NaCl as the precipitant. It was found that the best diffraction occurred by mixing 200mg/ml of lysozyme with 2.0M of NaCl in a 1:1 ratio. Powder diffraction data was collected at $\lambda=0.7\text{\AA}$ on NSLS (National Synchrotron Light Source) beamline X3B1 in similar condition to the data previously reported and is compared here:



Comparison of the diffraction peaks relative to the background for both patterns indicates that better powder diffraction data has been obtained for lysozyme. It is particularly evident at the higher two-theta value where diffraction peaks are still visible.

Subsequently, powder diffraction data was collected for two ranges of two-theta (4-5, 13-14). Powder samples were produced from lysozyme and lysozyme bound to N-acetylglucosamine. Calculation of Pearson correlation between diffraction suggests that the powder data could be grouped according to the bound and unbound lysozyme.

So far the results indicate that powder diffraction could potentially be used for screening. Further analysis is in progress to identify the quality of the diffraction data.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$45,000 |
| FY 2004 (budgeted) | \$80,000 |

Element-Resolved Dynamics of Nanoscale Ferromagnets

Chi-Chang Kao

03-121

D. A. Arena

PURPOSE:

The dynamical properties of magnetic thin films is of increasing importance with the emphasis to develop ever-smaller and faster hard drives, advanced magnetic memory for computers and novel magneto-electronic components. A further complication is that the magnetic materials used in advanced read heads and other memory elements are becoming more complex in both structure and composition in order to achieve improved performance. However, most experimental probes of magnetization dynamics, such as ferromagnetic resonance (FMR), measure magnetic properties that are averaged across an entire sample. The purpose of this LDRD is to develop elementally resolved magnetization measurements in the ps time regime. Initially, the time-resolved experiments will be used to investigate the damping of precessional rotation of the magnetization in thin film samples of permalloy (Py, an alloy of $\text{Fe}_{20}\text{Ni}_{80}$). However, the techniques and expertise developed for the initial project can later be applied to measurements of other magnetic systems including engineered magnetic nanoparticles.

APPROACH:

X-ray magnetic circular dichroism (XMCD) is a standard synchrotron-based spectroscopic technique for examining the magnetization of thin-film samples with element specificity. To achieve time-resolved XMCD measurements, we must synchronize a fast magnetization pulse with the photon pulses at the National

Synchrotron Light Source (NSLS) and the Advanced Photon Source (APS). The magnetization pulse (rise time ~ 100 ps) is introduced onto a microwave co-planar waveguide, where a magnetic alloy thin film has been deposited at the central constriction in the waveguide. The microwave pulse initiates a rotation of the magnetization of the sample towards the applied field. The magnetization of the sample does not switch immediately, however, but rather it precesses around the applied field with a decaying amplitude. The decay rate can be modified with the addition of small amounts of rare-earth metals, such as Tb, into the alloy film. Standard FMR and similar techniques, however, cannot address directly issues related to the coupling mechanism between the constituents of the alloy.

With time-resolved XMCD, we expect to follow separately the magnetization of the Fe, Ni and Tb in the film. For detection of the signal, we will proceed along parallel tracks and initiate measurements in a reflection geometry as well as in an x-ray transmission architecture. With the time resolved XMCD measurements, we can investigate questions that involve issues such as a phase delay between the magnetic moments of the Fe, Ni and rare earth (RE) atoms, or completely different dynamical behavior of the constituents of the alloy film.

To expedite the development of this project, we will collaborate with Prof. William Bailey of the Department of Applied Physics of Columbia University. Prof. Bailey is a pioneer in the field of time-domain microwave induction measurements and his laboratory will also grow the initial films that we will use in the experiments.

TECHNICAL PROGRESS AND RESULTS:

Hired a post-doctoral research associate in July 2003. Since then, the experimental design has been refined, and several critical components have been purchased. In addition, plans are underway for conducting initial measurements in December at the APS at Argonne National Lab. The time structure of the photon pulses at the APS is short enough to allow for standard pump-probe techniques to examine the magnetization dynamics in the time domain. Initially, this will simplify the structure of the experiments.

The detection scheme at the NSLS will be more sophisticated, as the photon pulses at the NSLS are too long to be used in a standard pump-probe configuration with ps time resolution. Nevertheless, suitable detection architecture, involving a fast photon detector (a Hamamatsu multi-channel plate with 150 ps rise time) has been developed and is currently being implemented.

Development of an appropriate co-planar waveguide is another high-priority task. Different architectures and substrates are necessary for the reflectivity and transmission modes of the experiment. Appropriate suppliers have been identified for these components and design efforts are progressing.

The majority of the electronics required for producing the fast magnetization pulses have been identified. In particular, a custom pulser with <100 ps rise time and a repetition rate of ~50 MHz has been specified, ordered and delivered. The pulser has undergone acceptance testing at Columbia University to verify the rise time.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$30,000 |
| FY 2004 (budgeted) | \$80,000 |

Membrane Biophysics Using Model Membranes

Ronald Pindak
L. Yang

03-122

PURPOSE:

Structural studies on biological membranes are important to understand the function and regulation of membrane proteins and other membrane structures that carry out important biological functions. However, unlike soluble proteins that can be crystallized and studied at atomic resolution, these membrane structures are normally fluid and cannot be crystallized. This LDRD project aims to explore different forms of model membranes that are suitable for studying membrane structures and establish the infrastructure that is needed to characterize these structures.

APPROACH:

The model systems to be explored in this project are solid supported multi-bilayers, solid supported single bilayers and freestanding multi-bilayers. Model systems that consist of pure lipid, as well as those that contain membrane active antimicrobial peptides will be studied. Under appropriate environmental conditions (temperature and hydration), these peptides are known to insert into lipid bilayers and collectively self-assemble into pores that are a few nm in diameter.

All the model systems will be studied by x-ray scattering using the synchrotron beam at The National Synchrotron Light Source (NSLS). However, since these model systems will be either 2-dimensional fluids or 2-dimensional crystals, optimized instrumentation must be developed to measure these weakly scattering, less

ordered structures. The single-layered lipid membrane will also be studied with the Atomic Force Microscope (AFM). The AFM studies will be performed either in collaboration with Dr. Sung-Ik Yang in Chemistry or using the AFM to be acquired by the NSLS-Physics soft condensed matter group.

The membrane structures are sensitive to environmental temperature and humidity. Therefore, an important part of this project is the design, construction and testing of sample chambers that can work with the x-ray instrument and AFM with accurate environmental control.

TECHNICAL PROGRESS AND RESULTS:

The research during the past year focused on solid supported model membranes. A sample chamber that can be mounted on the x-ray scattering setup at beamline X21 was constructed. This sample chamber not only controls temperature and humidity over a wide range, but also provides all the degrees of freedom that are needed to effectively perform x-ray scattering experiments. A recent modification to the chamber also allowed the fabrication of freestanding films directly inside the chamber. We have successfully prepared freestanding films of both pure lipid and a lipid-peptide mixture (Figure 1).

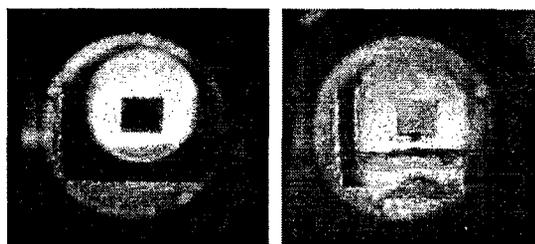


Figure 1. The image of the substrate before (left) and after (right) the film was spread over the 2mm x 2mm aperture.

A series of measurements have been performed using this sample chamber. In particular, the measurements performed on diphytanoylphosphatidylcholine (DPhPC) and phatidylcholine / dioleoylphosphatidyl-ethanolamine (DOPC/DOPE) mixtures have led to the observation of two new lipid phases (see Figure 2) that have important implications on the energetic pathway of membrane fusion.

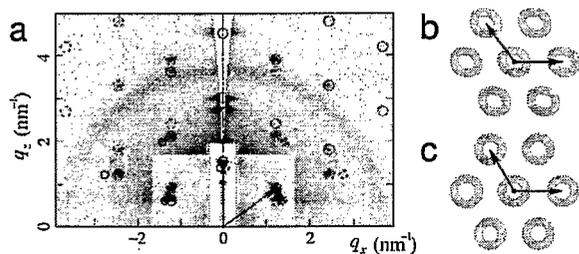


Figure 2. One of the newly observed lipid phase in DOPC / DOPE mixture. The diffraction pattern (a) indicates that the underlying structure is most likely composed of distorted lipid tubes, in contrast to the often-observed circular tubes. This implies that lipid sorting/de-mixing can be a mechanism of promoting membrane fusion.

The first AFM measurement on samples in the form of substrate supported single bilayer of pure lipid was performed. The sample preparation procedure is currently being optimized in order to integrate peptides into the bilayer.

We have recently hired a research associate, Masafumi Fukuto from Harvard University, to arrive in January 2004. Our research is therefore expected to expand significantly in the coming fiscal year, particularly in the area using single-layered lipid membrane. This research will be greatly facilitated by a beamline upgrade at X21 that will be completed in the spring 2004 and result in a factor of ~400 increase in the flux available at the sample. This high x-ray flux is necessary in order to conveniently study

single-layered membranes with extremely small sample volume (~5nm thick). There will also be more time available for AFM studies because of the arrival of the new AFM (PicoPlus, Molecular Imaging Inc., ordered in October 2003, to arrive in December 2003) in the soft condensed matter group. We therefore expect to accomplish the following milestones during FY 2004:

1. X-ray scattering measurements on crystalline and fluid two-dimensional structures in single layered model membrane.
2. Construction of AFM environmental chamber and AFM measurements on antimicrobial peptide assemblies under pore-forming conditions.

SPECIFIC ACCOMPLISHMENTS:

L. Yang and H. W. Huang, "A Rhombohedral Phase of Lipid Containing a Membrane Fusion Intermediate Structure," *Biophys. J.*, 2003 84:1808-1817

L. Yang, L. Ding and H. W. Huang, "New Phases of Phospholipids and Implications to the Membrane Fusion Problem," *Biochemistry*, 2003 42(22):6631-6635

L. Ding, L. Yang, T. M. Weiss, A. J. Waring, R. I. Lehrer and H. W. Huang, "Interaction of Antimicrobial Peptides with Lipopolysaccharides," *Biochemistry*, 2003 42(42):12251-12259

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$30,000 |
| FY 2004 (budgeted) | \$80,000 |

High Pressure in Strongly Correlated Materials – An Optical Investigation

Christopher Homes

03-127

PURPOSE:

The goal is to study the effect of pressure on the complex optical properties of highly-correlated electronic systems, and to look for novel behavior. The use of the diamond anvil cell (DAC) in optical high-pressure studies is a rapidly expanding field. However, much of this work has focused on insulating materials, such as minerals. Poorly conducting systems should be quite sensitive to changes in pressure (i.e. metal-insulator transitions, etc.) due to the poor screening and the possibilities for correlated behavior. The primary objective is to devise a reliable method for measuring the reflectance and transmission of the material and to then determine the complex optical properties. This has a high degree of technical difficulty, and it is not clear that we will be successful.

APPROACH:

Studies of highly-correlated materials are numerous, but there is little in the way of high-pressure optical work. We have encountered numerous problems in spectroscopy where there appear to be accidental degeneracies that might be removed with the application of pressure. This served as a motivation to attempt an in-house solution.

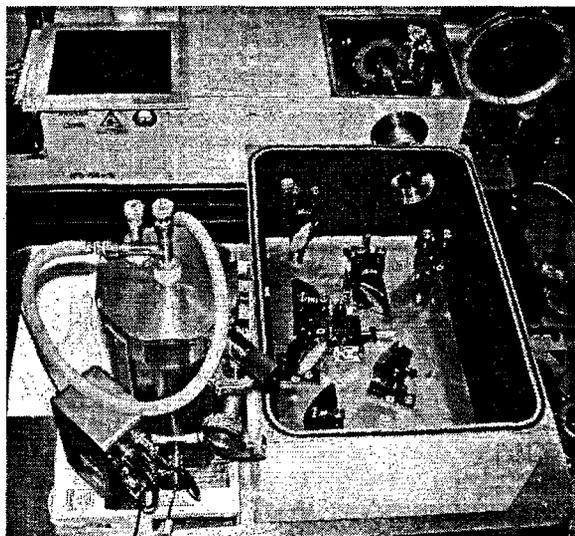
While diamond is the almost perfect optical window, the small gasket (or aperture) size in the DAC's makes it difficult to pass light through the cell. However, the NSLS provides an extremely bright source; through the use of optics that demagnify the image

size, it is possible to pass a significant amount of light through a small (100 micron) aperture. The combination of such an ideal source, and the expertise in infrared spectroscopy and reflecting optics suggested the viability of this project.

The high-pressure studies performed by the Materials Synthesis Group (T. Vogt) allowed us to exploit an existing knowledge base, rather than begin from scratch. In addition, this collaboration also gave us the opportunity to examine new materials.

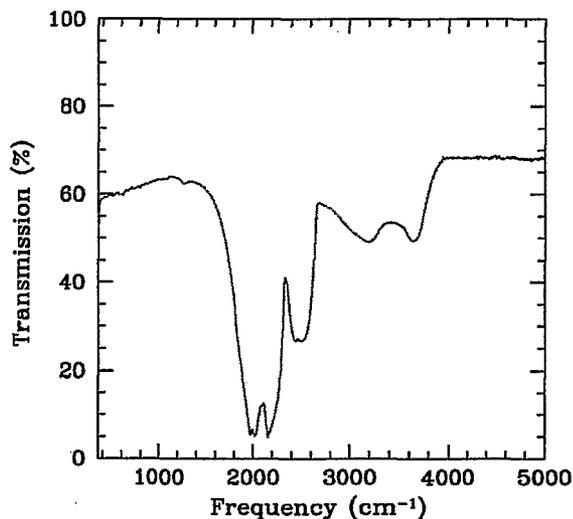
TECHNICAL PROGRESS AND RESULTS:

One of the first actions was to hire a postdoctoral fellow, Dr. Sasa Dordevic, who arrived in December of 2002. Subsequently, a DAC suitable for optical studies with type IIa diamonds was purchased and an optical system was designed using off-axis parabolic (OAP) mirrors for measuring the optical properties in a transmission geometry. The optical bench is shown below in a vacuum box attached to the Bruker IFS 66v/S spectrometer at NSLS beamline U10A.



The optics have been tested with a DAC in a vacuum bench with a synchrotron source;

the plot below shows resulting transmission through one of the diamond anvils in the cell – this indicates that with the exception of a narrow region between 2000-2200 cm^{-1} , a large spectral range is available for study.



The construction of the optical bench has allowed us to examine the infrared properties of various pressure-transmitting media at about 12 kbar (ruby calibration). We initially had wanted to use water-ethanol as a medium for examining the vibrational properties of water in zeolites. However, this mixture is nearly opaque in the infrared, suggesting that measuring the zeolites will be difficult to pursue. Better choices for pressure transmitting media appear to be kerosene, fluorinated mineral oils, and KBr (the latter is currently being used). In addition, we have also determined that we can use the infrared vibration lines of α -quartz powder as an internal pressure calibrant rather than ruby. This is an advantage, as we will no longer have to use ruby or a class 3b laser to calibrate the cell.

Planned work for the next year will include the construction of optics to measure the

reflectance of materials in a DAC using Schwarzschild optics, and to also attempt the use of imaging optics to resolve the spot on the sample. Measurements will be performed on the high-dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and highly correlated electronic systems.

SPECIFIC ACCOMPLISHMENTS:

Sum rules and energy scales in the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. C. C. Homes, S. V. Dordevic, D. A. Bonn, Ruixing Liang and W. H. Hardy, accepted for publication in Phys. Rev. B.

Energy scales in the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. C. C. Homes, S. V. Dordevic, D. A. Bonn, Ruixing Liang and W. N. Hardy, to appear in J. Superconductivity.

Signatures of bilayer splitting in the c -axis optical conductivity of double layer cuprates. S. V. Dordevic, E. J. Singley, J. H. Kim, M. B. Maple, T. Room, Ruixing Liang, D. A. Bonn, W. N. Hardy, J. P. Carbotte, T. Timusk, C. C. Homes, M. Strongin and D. N. Basov, submitted to Phys. Rev. B.

Pressure induced suppression of the singlet insulator phase in BaVS_3 : infrared optical study. I. Kezsmarki, G. Mihaly, R. Gaal, N. Barisic, H. Berger, L. Forro, C. C. Homes, and L. Mihaly, submitted to Phys. Rev. Lett.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$54,400 |
| FY 2004 (budgeted) | \$65,000 |

Polyoxometalate Giant Molecules: Novel Synthetic Methods, Characterizations and Potential Applications

Tianbo Liu

03-129

PURPOSE:

The purpose of this LDRD project is to study the new physical properties of giant polyoxomolybdate (POM) molecules. The important fundamental scientific problem is: "When the size of single inorganic molecules reach the order of nanometers, what new sciences can we expect?" In particular, we will focus on the unique solution properties of the giant POM anions. This proposal fits in well with BNL's efforts on nanoscience and soft condensed matter physics.

APPROACH:

Since last decade, inorganic chemists have continuously synthesized giant Polyoxomolybdate (POM) molecules, pushing the size of inorganic compounds to the nanometer scale. (The largest one was discovered by the principle investigator (PI) at BNL). However, their physical properties have not been systematically studied. In the fields of nanoscience, the giant POMs offer a "dual personality" benefit: they possess the advantages of single molecules (well-defined structures and uniform size and mass) and those of nanoparticles (complex and variable electronic, magnetic, and colloidal properties). This combination of properties, especially the molecules' monodispersed nature and adjustable chemical and physical properties, could help to develop more diverse nanomaterials than were previously thought possible.

The first priority is to study the fascinating solution behavior of these giant POM anions, which provides a valuable link to connect

those of simple ions, polyelectrolytes (e.g. proteins and deoxyribonucleic acids (DNAs) and hydrophilic colloids.

Laser and small-angle X-ray scattering techniques and transmission electron microscopy (TEM) (H. Li, Biology, BNL) are used for the study. Some samples were provided by Prof. Achim Müller of the University of Bielefeld, the leading synthetic chemist in the field of POM.

TECHNICAL PROGRESS AND RESULTS:

We successfully determined the supramolecular vesicles structure in POM solutions, leading to the discovery of a new type of self-assembly in nature and finally solved the historical "blue water" puzzle. A new universal solute state has been identified, leading to the opening of a new field. A lot of new physical phenomena have been discovered.

We are also studying the unique magnetic properties of POM-based giant molecules, which could find new applications in biomedical fields.

We will continue to explore the new physical properties on nanoscaled inorganic molecules in the next fiscal year.

SPECIFIC ACCOMPLISHMENTS:

Tianbo Liu*, Ekkehard Diemann, Huilin Li, Andreas Dress, and Achim Müller, "Self-Assembly in Aqueous Solution of Wheel-Shaped Mo₁₅₄ Oxide Clusters into Vesicles," *Nature*, 2003, 425, in press.

Tianbo Liu*, "An Unusually Slow Self-Assembly of Giant Inorganic Ions in Aqueous Solution," *J. Am. Chem. Soc.*, 2003, 125, 312-313.

Tianbo Liu*, "Supramolecular Structures of Polyoxomolybdate-Based Giant Molecules in

Aqueous Solution,” *J. Am. Chem. Soc.*, 2002, 124, 10942-10943.

Tianbo Liu*, “Surfactant-Induced Trans-Interface Transportation and Complex Formation of Giant Polyoxomolybdate Clusters,” *J. Clust. Sci.*, 2003, 14, 215.

Tianbo Liu*, Brandon Imber, Hartmut Bögge, Raul Tomsa, Huilin Li, Zhiqiang Chen, Joris van Slageren, and Achim Müller*, “Stepwise Tuning the Charge of Well-Defined Nanobjects with the Property of Assembling to Vesicles Leads to Charge Dependent Tuning of Size,” submitted to *Science*.

Tianbo Liu*, “Giant Inorganic Ions in Dilute Solution: Equilibria and Transitions Between the First and the Second Solute States and Determination of the Activation Energy,” submitted to *J. Am. Chem. Soc.*

Tianbo Liu* and Achim Müller*, “Novel Vesicle Assemblies: Unusual Behaviors of Nanometer Scale Inorganic Ions” (feature article), *ChemComm.*, submitted.

Tianbo Liu*, Ekkehard Diemann, and Achim Müller*, “New Physics Emerge from An Old Puzzle – What Happens When Inorganic Ions Reach the Size of Nanometer Scale?” (invited paper), *J. Chem. Edu.*, submitted.

Guang Liu, Matthew Cons, and Tianbo Liu*, “The Ionic Effect on Supramolecular Aggregates in Polyoxomolybdate Solution,” *J. Mol. Liq.*, submitted.

The achievements were also widely reported in top scientific public magazines in different countries:

“Singin’ the Blue,” *Chemistry – American Chemical Society’s Award-Winning Publication*, pp. 4, Winter 2003.

“Magnetic Molecules Take Better Pics – Sharper Scans Out of the Blue,” *New*

Scientist, vol. 175, issue 2359, pp. 17, 2002 (U.K., U.S.A.).

“Molybdän und Brombeersöße”, *Wissenschaft-online* (German edition of the Scientific American).

“Researchers Track New Solute State,” *Tcetoday* (U.K.).

“Old Chemical Enigma Solved,” *Popular Mechanics*, pp. 34, December Issue, 2002.

“Molibdénkékkel,” *Nepszabadsag* (Hungary), January 18th, 2003.

Symposium organizer and Chair (from polyoxomolybdate to complex ions), 28th International Conference on Solution Chemistry, Debrecen, Hungary, August 23-28, 2003. This special mini-symposium is set to discuss my recent results with other scientists.

“Discovery of a new solute state – new sciences emerge when inorganic molecules reach nanometer scale,” American Chemical Society’s (ACS’) National Meeting in New York, September 9, 2003 (Invited talk).

Four high school students have been working with me during the summer. They have been very successful in various national competitions.

Branson Imber: Intel finalist (top 40 in the nation); Siemens-Westinghouse semifinalist; Champion, Long Island Science Fair (physics); Champion, Naval Research Contest.

Clara Tow: Intel semifinalist (top 300 in the nation); Siemens-Westinghouse semifinalist.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$ 54,000 |
| FY 2004 (budgeted) | \$100,000 |

Exploratory Sol-Gel Synthesis

Thomas Vogt
Sangmoon Park

03-135

PURPOSE:

The goal of this LDRD is to advance synthesis capabilities, in particular, using sol-gel and solution-based chemistry.

APPROACH:

We have concentrated our efforts on four main areas:

- (1) A new family of inorganics phosphors,
- (2) Sol-gel routes to nanostructured materials with high dielectric constants,
- (3) Selective Ion Layer And Reaction (SILAR) thin film deposition,
- (4) Novel synthesis routes for 'soft' superconductors in the $A_x(MO_2) \cdot nH_2O$ family.

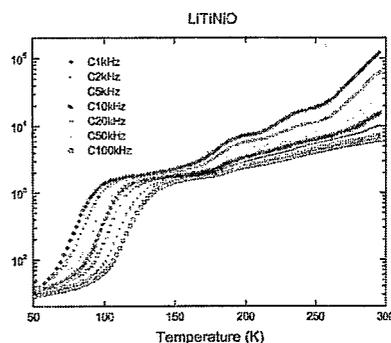
Main collaborators are C. C. Homes and W. Si (Physics, BNL), Jim Misewich (Department of Material Sciences (MSD), (BNL)), Perena Gouma (Material Science and Engineering (MS), State University at Stony Brook (SUNYSB)), Pat Woodward (The Ohio State University), Hanno zur Loye (University of South Carolina).

TECHNICAL PROGRESS AND RESULTS:

- (1) We have identified a new family of inorganic luminescent materials based on an ordered oxyfluoride framework structure of the general type $A(Al_{1-x}Ga_x)O_4F$. A wide spectrum of luminescence (red, green, blue) is accessible by adequate doping with rare earth ions.

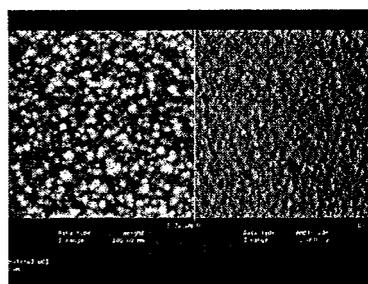


- (2) Sol-gel routes have been found to make $CaCu_3Ti_4O_{12}$ and doped NiO materials, which show giant dielectric constants likely to be due to inter barrier layer capacitance (IBLC) effects.



Above an example of the dielectric constant of Ti-doped NiO as a function of temperature is shown. We intend to use pulsed laser deposition to make films of these materials and investigate the break down voltage (Fowler-Nordheim tunneling) in these materials in collaboration with Jim Misewich (MSD, BNL).

- (3) We have been able to come up with a SILAR route ("Selective Ion Layer And Reaction") to make TiO_2 films. TiO_2 films find a large variety of applications (solar cells, optical wave guides, gas sensors, electrochromatic displays, self-cleaning window and self-sterilizing surfaces). We are currently investi-gating the catalytic properties (M. White, University of Texas) and the gas and bio sensing capabilities (P. Gouma, SUNYSB). Tim Kid, Condensed Matter Physics (CMP), is perusing X-ray Photoelectron Spectroscopy (XPS) work in collaboration with Laura Lewis, Department of Material Sciences (MSD), provides us access to an atomic force microscope (AFM).



(4) The observation of superconductivity in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ at 5K sparked interest in this system since it is only the second class of systems where superconductivity arises from doping a Mott insulator. It was realized early on that these materials are (a) sensitive to variations of their water content when handled without special precautions in the atmosphere and (b) the original synthesis relied on using bromine in acetonitrile (flashpoint 42 F). We have found an alternative synthesis route, which allows us to make large quantities of sample, is environmentally benign and uses only water as solvent. We have also made, for the first time, the non-superconducting Li-analog (cannot be made using original synthesis route). This provides us a 'soft synthesis' route for a variety of materials in the $\text{AMO}_2 \cdot n\text{H}_2\text{O}$ family. We are currently exploring transport properties of a variety of these now accessible materials.

SPECIFIC ACCOMPLISHMENTS:

Awards:

MSA Crystallographic Research Grant Award (2004), Mineralogical Society of America.

Publications:

Park, S.; Lee, Y.; Moodenbaugh, A.; and Vogt, T. (in press). *Synthesis and high-pressure behavior of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and related phases*. Phys. Rev. B. Rapid Communication.

Patents:

A New Family of Inorganic Luminescent Materials, Vogt, T.; Park, S.; Woodward, P. M. Invention disclosure submitted.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$75,000 |
| FY 2004 (budgeted) | \$82,000 |

In Situ Soft X-ray Absorption Spectroscopy Studies of Cathode Materials for Thin Film Lithium-Ion Batteries

Won-Sub Yoon

03-137

M. Balasubramanian

PURPOSE:

The objective of the proposed research is to explore the redox behavior and electronic properties of cathode materials used in lithium-ion batteries and to develop the scientific methodology to obtain high quality data using in situ soft X-ray absorption spectroscopy (XAS) during electrochemical cycling. In order to develop high performance Li-ion batteries, it is necessary to understand the charge compensation mechanism of Li-ion batteries during the charging and discharging process. This research will aid in the rational design of electrode materials for Li-ion batteries with high performance.

APPROACH:

It is traditionally assumed that in a lithium/metal-oxide compound used as a cathode material in batteries, the transition metal atom changes valence on Li intercalation/deintercalation. This assumption comes from the belief that in transition-metal oxides, the cation d levels are just above the oxygen 2p band and that the Fermi level is set primarily by the cation d levels. However, recent theoretical calculations by Ceder et al.'s group at the Massachusetts Institute of Technology (MIT), strongly suggests that such a simple model of charge compensation is naïve. Their calculations suggest that for late transition metal oxides (such as Ni-based oxides) it is the oxygen that is largely responsible for charge

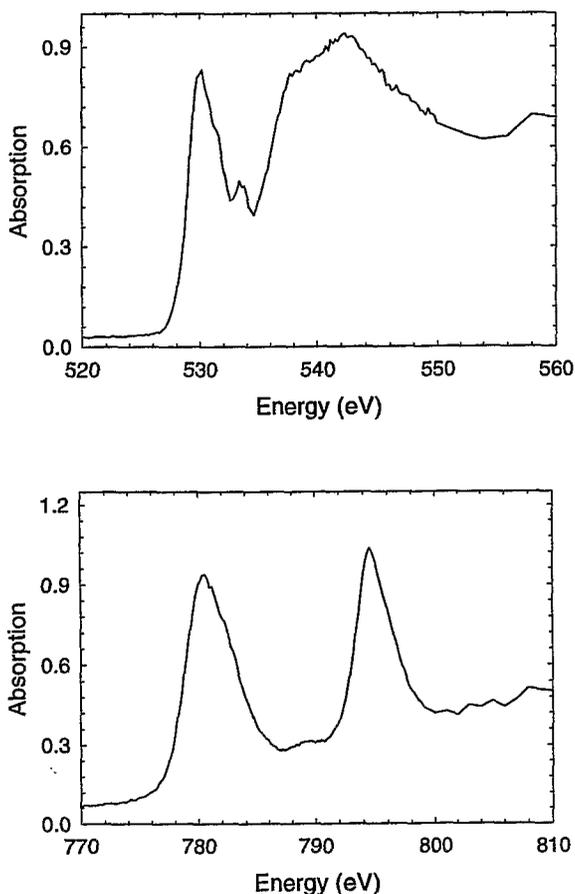
compensation. In transition metal oxides, the multiplet structure of the L-edge (2p) XAS of the transition metal provides information on the ground state electronic configuration (oxidation state and spin) of the probe atom. The O K-edge (1s) spectra gives information on the nature of the bonding and charge distribution between the O and the transition metal. Combined together the O 1s and the transition metal 2p XAS will be a powerful tool to understand the redox processes and charge compensation mechanisms in the cathode material as a function of the state of charge. We used soft XAS at O K-edge and transition metal L-edge at beamline U7 at the National Synchrotron Light Source (NSLS). We are developing an in situ thin film spectroelectrochemical cell in collaboration with scientists at City University of New York (CUNY) and Jet Propulsion Laboratory (JPL). Collaborators include D. Fischer, National Institute of Standards & Technology (NIST), C. -C. Kao (BNL), M. denBoer, (CUNY), J. F. Whitacre (JPL), and J. McBreen (BNL).

TECHNICAL PROGRESS AND RESULTS:

Investigations to test the thin Si₃N₄ window (proposed window material for the spectroelectrochemical cells) have been completed and ex situ studies on a number of different cathode materials of interest have been performed.

The following figures show O K-edge and Co L_{III,II}-edge XAS spectra of LiCoO₂ using a 100 nm thick Si₃N₄ window. Major peak features in both spectra are consistent with previous reports. The intense absorption peak below, 535 eV in the O K-edge spectrum of the LiCoO₂, represents the transition of oxygen 1s electron to the hole state in the oxygen 2p level hybridized with Co 3d orbitals. The broad higher energy

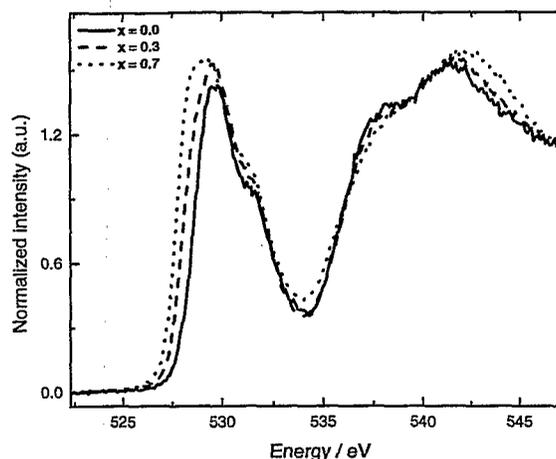
peaks above 535 eV can be assigned to the transitions to hybridized states of oxygen 2p and Co 4sp orbitals. The Co $L_{III,II}$ -edge shows main peaks at ~ 781 eV and ~ 795 eV, which are due to electronic transitions of Co $2p_{3/2}$ and $2p_{1/2}$ core electrons, split by the spin-orbit interaction of the Co 2p core level, to an unoccupied 3d level highly hybridized with oxygen 2p orbital, respectively.



The electronic structure for an electrochemically deintercalated $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$ electrode has been investigated intensively with ex situ soft XAS at the O K-edge, and the metal $L_{III,II}$ -edges. Mn and Ni $L_{II,III}$ -edge XAS results indicate that charge compensation in the bulk during charge is achieved mainly by the oxidation of Ni^{2+} to Ni^{4+} ions. Changes in the features on the low energy side of pre-edge peak at the O K-

edge at higher states of charge indicate that the holes compensating lithium ion deintercalation are located in O 2p states as well as Ni 3d states.

The following figure shows O K-edge XAS spectra of electrochemically Li-ion deintercalated $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ system. As for the pre-edge intensity, the spectral weight increases by $\sim 35\%$ from $x = 0$ to $x = 0.7$ in $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ compared to that of pristine $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, indicating that the large portions of the holes that compensate the lithium ion deintercalation are located in O 2p states.



Our studies have proven FY soft XAS is an excellent technique for investigating the charge compensation mechanism in the Li-ion intercalation-deintercalation process of cathode materials for Li rechargeable batteries.

We plan to complete the development of the scientific methodology to obtain high quality data using in situ soft X-ray absorption spectroscopy (XAS) during electrochemical cycling and expand the work to other transition metal oxide systems and to mixed metal oxide systems. In mixed metal oxide systems, the order in which a particular metal is oxidized will be probed.

SPECIFIC ACCOMPLISHMENTS:

Publications:

D. P. Abraham, R. D. Twisten, M. Balasubramanian, J. Kropf, D. Fischer, J. McBreen, I. Petrov, and K. Amine, "Microscopy and Spectroscopy of Lithium Nickel Oxide-Based Particles Used in High Power Lithium-Ion Cells," *J. Electrochem. Soc.* 150, A1450 (2003).

W. -S. Yoon, M. Balasubramanian, X. -Q. Yang, Z. Fu, D. A. Fischer, and J. McBreen, "Soft X-ray Absorption Spectroscopic Study on the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ Cathode Material during charge," *J. Electrochem. Soc.*, accepted.

W. -S. Yoon, C. P. Grey, M. Balasubramanian, X. -Q. Yang, D. A. Fischer, and J. McBreen, "A Combined NMR and XAS Study on the Local Environments and Electronic Structures of the Electrochemically Li-ion deintercalated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode System,"

Electrochemical and Solid-State Letters, accepted.

Presentations:

W. -S. Yoon, X. -Q. Yang, M. Balasubramanian, and J. McBreen, "Soft X-ray Absorption Spectroscopic Studies of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ for Li Rechargeable Batteries," 204th Electrochemical Society Meeting, Orlando, Florida, USA, 2003.

J. McBreen, M. Balasubramanian, X. -Q. Yang, H. -S. Lee, W. -S. Yoon, A. Moodenbaugh, D. A. Fischer, Z. Fu, and D. Abraham, "Synchrotron X-Ray Studies of the Solid Electrolyte Interface on Cycled Lithium-ion Battery Electrodes," 204th Electrochemical Society Meeting, Orlando, Florida, USA, 2003.

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$80,000 |
| FY 2004 (budgeted) | \$83,000 |

Functional Bulk Mn-Based Nanocomposites

Laura H. Lewis
C.-C. Kao

03-138

PURPOSE:

The objective of this work is two-fold: scientific and strategic. The scientific objective is to synthesize and characterize novel bulk nanocomposites composed of ferromagnetic nanoparticles of MnBi (or MnSb) embedded in a nonmagnetic matrix of Bi (or Sb). This combination of phases has not heretofore been investigated, and it is anticipated that the nanocomposite will exhibit unusual magnetic phenomena such as enhanced ferromagnetism, a significant magneto-optical Kerr effect, a large magnetocaloric effect, and a giant magnetoresistive effect. It is likely that the system's magnetic transition temperature and anisotropies will differ from those found in the bulk analogue. The scientific objective supports the Energy Strategic Goal of the Department of Energy (DOE) by promoting efficient delivery of energy, as well as, the Science Strategic Goal of the DOE by providing world-class scientific research capacity and advancing scientific knowledge. The strategic objective of this work is to enhance the materials synthesis capabilities resident in the Materials Science Department by the installation and utilization of a commercial Melt Spinner, which is a specialized piece of equipment for non-equilibrium solidification synthesis and processing.

APPROACH:

Synthesis techniques of melt-spinning and *ex-situ* annealing have been selected to obtain kinetically-stable MnBi (or MnSb)

phase of the low-temperature phase (LTP) type at room temperature: the initial charges for melt-spinning have been prepared, and the as-melt-spun sample will be in the form of ribbons consisting of a metastable solid Mn-Bi solution.

Basic structural characterization of the melt-spun materials will be achieved by standard laboratory x-ray diffraction and transmission electron microscopy (TEM) to ascertain the phase content, distribution and dimensional scale. More detailed structural characterization will be carried out using high-resolution TEM (in collaboration with Yimei Zhu, BNL) and atomic force microscopy. Properties to be investigated include uniformity of particle size and interparticulate interactions. Characterization of the magnetic properties of the nanostructure will be carried out with bulk magnetic measurement of the intrinsic and extrinsic magnetic properties: saturation magnetization, magnetic blocking and Curie temperature, coercivities and magnetocaloric effects. For this, the static (*dc*) and dynamic (*ac*) magnetic responses of the materials will be probed with superconducting quantum interference device (SQUID) magnetometry. Lorentz TEM, and magnetic force magnetometer will be utilized to verify the nature of the interphase interface and the magnetic domain configuration. Advanced characterization of the phase constitution, structure scale and magnetic attributes of the nanodispersed particle size distributions will be accomplished with specialized synchrotron methods such as x-ray magnetic circular dichroism (XMCD) as well as x-ray diffraction and x-ray small-angle scattering.

TECHNICAL PROGRESS AND RESULTS:

The commercial Melt Spinner (Edmund-Buhler GmbH, model SC) was delivered in April 2003. Installation of the equipment in

Bldg. 480 required significant modification to the existing space, such as rewiring of the power cables and installation of multiple lines for cooling water. Hired a post-doctoral researcher, Dr. Kyongha Kang, who arrived at BNL in July. At the current time, the Melt Spinner is installed and operational but has not yet passed its safety requirements for radio frequency (RF) radiation. We are currently interacting with the BNL Industrial Hygiene (IH) group for RF surveys. We are confident that Melt Spinner operation will start by December 2003. At that time, we will proceed with the synthesis and characterization of the MnBi and MnSb nanocomposite alloys.

Synthesis of the master MnBi alloy is underway and preliminary results are available. Initial charges for melt-spinning have been obtained by heating the elements of ratio 55 at% Bi-45 at% Mn to 1050 °C in an evacuated sealed vitreous silica tube, backfilled with 0.25 atm Ar. The alloy was held at temperature for 5 days and slowly cooled to room temperature. The x-ray diffraction pattern for the sample is shown in Figure 1. X-ray powder diffraction patterns for Bi, Mn low-temperature phase (LTP) QHTP MnBi with segregated Bi are presented. The LTP MnBi can also be seen. As expected, the alloy is mainly composed of MnBi; the quenched high-temperature phase (QHTP), MnBi are also presented as references.

The synthesis process needs to be optimized, both for appropriate chemical composition of the master alloy and the melt-spinning conditions, such as wheel speed, ejecting gas

pressure, etc. In particular, the magnetic phase particle size may depend on the volume ratio of each element. *Ex-situ* annealing of the quenched nanocomposite will control the structure of the materials and thus their magnetic properties. The annealing temperature plays an important role in determining the stable phase obtained after the annealing. A relatively low annealing $T < 260$ °C will be used to obtain LTP MnBi. The annealing time, as well as, the annealing temperature is an important factor that determines the MnBi nanoparticle size. Appropriately sized MnBi particles with a very high magnetic anisotropy will be fabricated using optimized processing conditions.

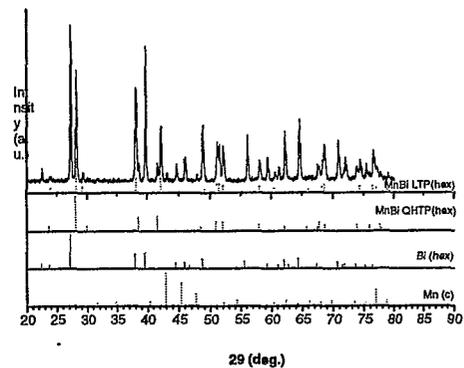


Figure 1. X-ray diffraction of Mn – 55 at % Bi master alloy

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$28,000 |
| FY 2004 (budgeted) | \$78,000 |

Nanostructured Transition Metal Oxides

Lijun Wu
M. Suenaga

03-144

PURPOSE:

Properties of crystalline solids are not normally classified according to size, but size begins to control and change crystal and electronic structures, thus fundamental characteristics at the scale of <10nm. We will investigate systematically the crystal and electronic structures of nanocrystalline cerium and transition metal oxides in order to understand the various factors controlling the changes in structure from those of the bulk materials.

APPROACH:

The cerium and transition metal oxide nanoparticles were synthesized using the technique of thermal evaporation in helium atmosphere. For transmission electron microscopy (TEM) observation, the particles were collected onto the lacy-carbon-coated side of the copper grids during the course of evaporation.

A 300KV JEOL-3000FEG TEM equipped with a Gatan Imaging Filter (GIF), an annular dark-field detector and an image-plate recording system was used to study crystal and electronic structures of cerium and transition metal oxides as a function of the particle size. The microscope can be operated in either TEM or scanning transmission electron microscope (STEM) mode. In general, TEM mode was used to obtain high-resolution images and diffraction patterns for the measurements of lattice parameter, while the STEM mode was employed to obtain electron energy-loss spectra (EELS) for individual particles. The probe size in STEM was approximately 0.13nm. The advantage of

using EELS in high resolution TEM and STEM is that a single nanoparticle can be examined and the size and crystal and electronic structure of that particle can be simultaneously determined. Moreover, with the 0.13nm probe size; we are able to clarify the surface effects for the nanoparticles.

Collaborators:

H. J. Wiesmann, Y. Zhu, D. O. Welch, A. R. Moodenbaugh, R. Klie (Department of Materials Science) and D. A. Fischer, National Institute of Standards & Technology (NIST).

TECHNICAL PROGRESS AND RESULTS:

In FY 2003, we have built a system based on the thermal evaporation technique to prepare nano-sized particles of cerium and transition metal oxides. A series of cerium oxide nanoparticles with diameters from ~3nm to ~20nm were obtained, with size controlled by helium gas pressure. Figures 1 (a-c) shows examples of high-resolution images of variously sized cerium oxide nanoparticles.

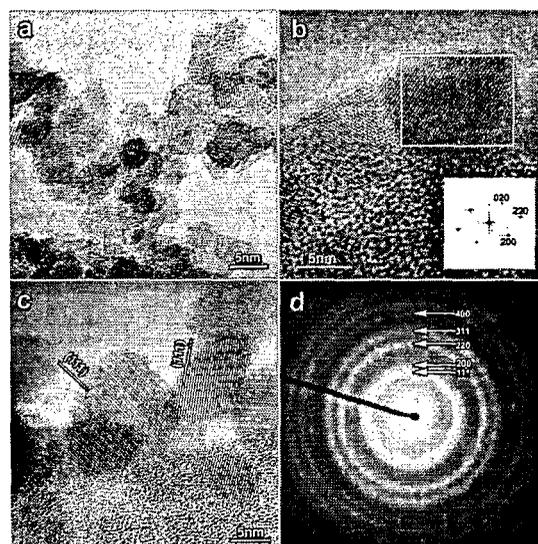


Figure 1. (a-c) Examples of high-resolution images of particles with different average sizes. The inset is the Fourier Transform from the marked area. (d) Electron diffraction pattern from (a)

Figure 1d shows a diffraction pattern taken from the particles shown in Figure 1a. Electron diffraction patterns and high-resolution images show that the crystal structure of cerium oxide nanoparticles is cubic with lattice parameter larger than that of bulk samples. A micromechanical model based on linear elasticity was used to explain the lattice expansion of the CeO_{2-x} nanoparticles.

EELS and X-ray absorption (XAS) in the M-edge (M_5 and M_4) region of rare-earth elements carry information on the initial state 4f occupancy, and thus can be used to evaluate the valence of the ions of the rare-earth elements. Initially, we used micron-size CeO_2 and $\text{Ce}_2(\text{WO}_4)_3$ particles to obtain the standard EELS spectra of Ce^{4+} and Ce^{3+} (the valences of Ce ions in micron-size CeO_2 and $\text{Ce}_2(\text{WO}_4)_3$ are nominally 4^+ and 3^+ , respectively). Figures 2 (a-b) show these EELS spectra. The intensity of the M_4 edge is higher than that of M_5 edge in Ce^{4+} and reversed in Ce^{3+} . Quantitative intensity ratios of M_5/M_4 are obtained by measuring the intensity of the M_5 and M_4 peaks in the second derivative of the spectra. The M_5/M_4 ratios are 0.91 for Ce^{4+} and 1.31 for Ce^{3+} from these "standard" large particles.

After successfully making a series of cerium oxide nanoparticles, we acquired a series of EELS spectra over a range of particle size. The EELS spectra from particles with diameters $d=11$, 6, and 3.5nm, are shown in Figures 2 (c-e), qualitatively illustrating a systematic change in the EELS spectra with the particle size. Detailed analysis indicates that the spectrum (Figure 2c) from a particle with $d=11\text{nm}$ is close to that of Ce^{4+} , while that (Figure 2e) for a 3.5nm particle is close to that of Ce^{3+} . In Figure 2f, quantitative measurements of M_5/M_4 ratio are summarized and plotted against particle size. It shows that the valence of Ce ions decreases with decreasing particle size.

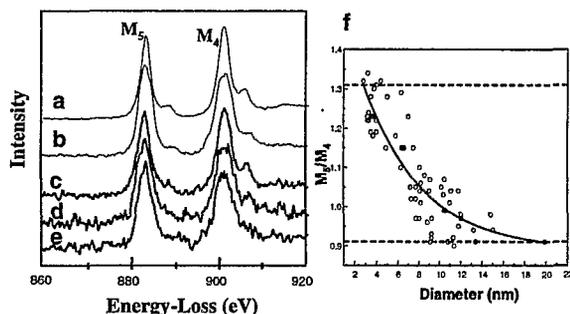


Figure 2. (a-e) EELS spectra of micron-size (a) CeO_2 and (b) $\text{Ce}_2(\text{WO}_4)_3$, and nano-size CeO_2 particles with (c) $d=11\text{nm}$, (d) $d=6\text{nm}$ and (e) $d=3.5\text{nm}$, respectively. (f) Dependence of the M_5/M_4 ratio on the particle size of CeO_{2-x} nanoparticles.

With the 0.13nm probe size in our TEM, we explored the possible local variations in the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio within a particle by selectively acquiring EELS spectrum from the edge (the surface) and the central region (the interior) for a given particle. This provides us an estimate of the volume fractions of cerium ions with 3^+ and 4^+ in the surface region and the interior of a particle. For particles greater than 3-4nm, a distinction between surface and bulk can be discerned. The valence of Ce ions in the interior of the particle is close to 4^+ , while that at the surface is close to 3^+ .

SPECIFIC ACCOMPLISHMENTS:

L. Wu, H.J. Wiesmann, A.R. Moodenbaugh, D.A. Fischer, Y. Zhu, and M. Suenaga. "Electron Energy Loss Spectroscopy of CeO_{2-x} Nanoparticles," was presented at the Microscopy and Microanalysis 2003 Meeting, Proceedings 820CD.

L. Wu, H.J. Wiesmann, A.R. Moodenbaugh, R. Klie, Y. Zhu, D.O. Welch, and M. Suenaga. "Oxidation State and Lattice Expansion of CeO_{2-x} Nanoparticles as a Function of Particle Size," Phys. Rev. B, (submitted).

LDRD FUNDING:

| | |
|--------------------|----------|
| FY 2003 | \$40,000 |
| FY 2004 (budgeted) | \$78,000 |

Radio Wave Detection of Ultra High Energy Cosmic Rays

Helio Takai

03-151

PURPOSE:

Physics in the energy scale of 10^6 TeV and beyond is only accessible today via the ultra high-energy cosmic rays. These are rare events, and large detection systems are required if one wants to pursue this avenue. At an event rate of $1/\text{km}^2/\text{year}$, detectors of the size of $10^5 - 10^6 \text{ km}^2$ would be required to make this idea viable. We propose to use a passive bi-static radar technique to detect these rare events. Radio waves are known to be Thompson scattered by the ionization produced in the atmosphere by meteorites and micrometeorites. Ultra high energy (UHE) cosmic rays produce similar ionization densities. However, the ionization lifetime and extent of the cosmic ray showers are significantly different than meteorites.

APPROACH:

The detection of UHE cosmic rays with $E > 10^{18}$ eV and beyond requires large detector arrays. Some examples of such detectors are the Akeno Giant Air Shower Array (AGASA) experiment in Japan with 100 km^2 and the Auger observatory now under construction with 3000 km^2 . To detect events above the Greisen-Zatsepin-Kuzmin (GZK) limit of 5×10^{19} eV, new techniques need to be developed to allow for the construction of larger area detection systems. Radio and radar techniques have received some attention recently due to the large areas that can be covered at reasonable cost. The direct detection of radio emission is one technique that has received attention

in the past few years. Active radar techniques have also received some attention but at theoretical levels. A passive bi-static radar technique has been used in the study of atmospheric phenomena but not attempted for cosmic rays. This project is setting up a mixed array of radio detectors and small shower arrays to detect in coincidence radio echo in the Very High Frequency (VHF) band and muons from extensive air showers. What makes the coincidence possible is the use of Global Positioning System (GPS) clocks with $1 \mu\text{s}$ accuracy or better. The radio stations will be located at BNL and two other sites. Shower arrays will be located at BNL and nearby high schools. (See Figure 1.)

Collaborators – Dr. Denis Damazio (research associate), Tara Falcone (SUNY-Stony Brook, Master of Arts in Teaching (MAT) student), Nishant Mehta (Cornell - Master student), Harry Themann (Graduate Student – SUNY-Stony Brook), Thomas Feierabend (radio consultant), Joseph Sundermier (Deer Park High School), Tania Entwistle (Ward Melville High School), and Bruce Qua (Longwood High School).

TECHNICAL PROGRESS AND RESULTS:

The first experimental setup was a radio station on the rooftop of Building 510. Two types of antennae were installed. A high gain directional antenna and a (nearly omnidirectional) low gain antenna. Multiple receivers for signal demodulation are available, and data can be recorded simultaneously in 6 different frequencies. The station has an independent GPS timeserver to keep the acquisition computer time synchronized to $1 \mu\text{s}$ to Universal Time (UTC). A computer system to record data for the entire experiment was purchased and installed. This station has a storage capacity of 2.5 Tbyte and 4 processors for the

extraction of relevant signals. It will be used to store data from radio stations and scintillator arrays. The data from the radio station is automatically uploaded to the main data acquisition computer on a daily basis. Analysis software was developed using signal processing techniques used in passive radar and sonar systems making use of spectral (frequency vs. time) maps. Offline triggering and feature extraction (signal peak, duration, reflected power) are performed. A second BNL station is now being setup in Building 438, Education Center. A sight evaluation for State University of New York at Stony Brook (SUNY-SB) was carried out in July but considered too noisy. The proximity to the hospital and WUSB radio station makes SUNY-SB a poor site for a radio station. Another site is now under consideration at the Peddie High School in Hightstown, NJ. (See Figure 1.)

A design for the shower array has been done, and a prototype is in operation for the past 3 months at BNL. The design uses four scintillator paddles of 0.25m^2 in area and in coincidence. The basic idea is to provide a way to detect only showers from cosmic rays of large energies. Monte Carlo simulations show that a threshold energy of 10^{16} eV is required to trigger a four-fold coincidence. The array was developed together with physics teachers that are part of this experiment. Arrays are now in construction, and we expect deployment to high schools by December 2004. The average rate of events measured is approximately 10 events/hour. This work will be part of Ms. Tara Falcone's MAT degree.

Simulation effort to calculate the form of the radio signal was initiated. Simulation code has been tested against published data. This

work will be part of the Master's work of Mr. Nishant Mehta from Cornell University. One of the main unknowns in the simulation is the free electron lifetime. An experiment is now under construction at the National Synchrotron Light Source to perform this measurement.

Analysis of the radio data collected so far shows a predominance of signals from meteorites and micrometeorites (Figure 2). The event rate has a 24h periodicity with a maximum at early morning hours (Figure 3). The analysis of coincidence data is now underway. As a first pass, an event time list is generated for the radio signals (for multiple frequencies) and for the shower detector. Off-line the information is combined and a search for time coincidence performed. First results should become available in the near future.

SPECIFIC ACCOMPLISHMENTS:

The preliminary results from the stand-alone radio station were presented as an oral contribution at the 2003 Institute of Electrical and Electronics Engineers, Inc. (IEEE) Nuclear Science Symposium and Medical Imaging Conference (2003 Nuclear Science Symposium/Medical Imaging Conference (NSS/MIC)).

A contribution to the Second International Conference on Particle and Fundamental Physics (in Washington, DC) was submitted and will be presented as a poster.

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$100,000 |
| FY 2004 (budgeted) | \$125,000 |

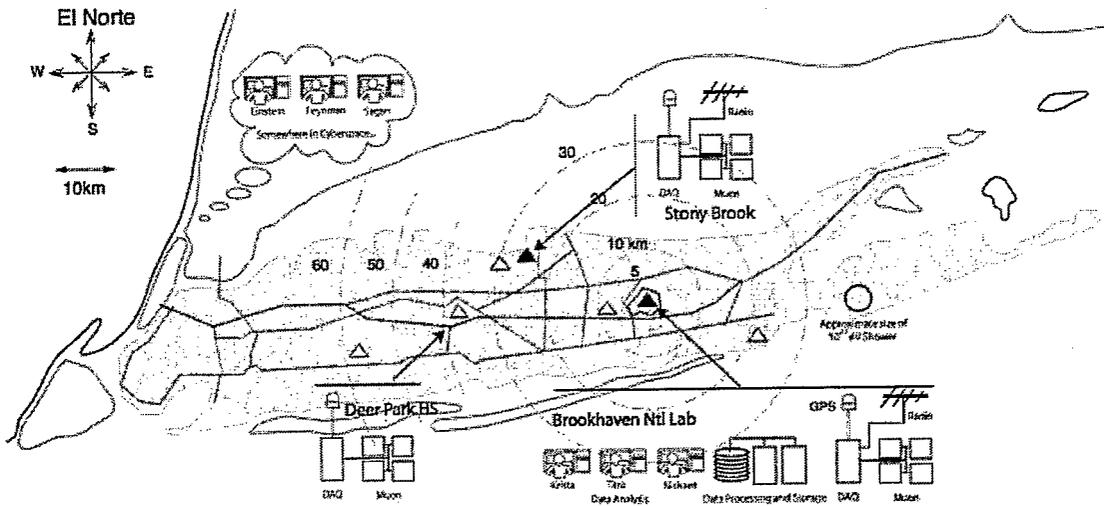


Figure 1. Layout of the cosmic ray experiment. The main radio station is located on BNL site. BNL site also hosts a small shower array and computer facilities to store the data from all sites. The Stony Brook site will have another shower array. The site was not qualified as a radio site because of the elevated levels of radio noise. White triangles indicate High Schools where shower arrays will be installed. Each site will have a GPS to tag the event time. A site in Hightstown, NJ is now under consideration for a radio station. The data will be available on the internet for people interested in the data.

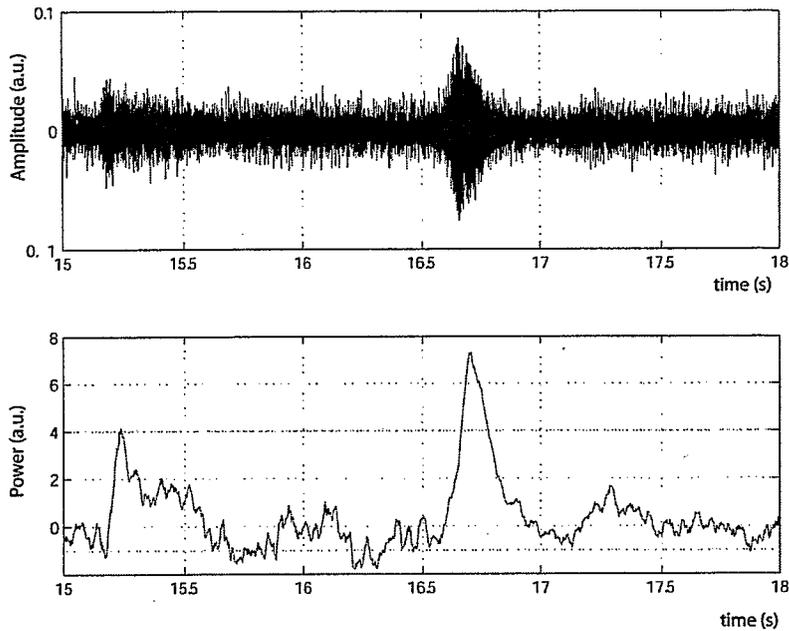


Figure 2. Raw digitized radio signal (top panel) and noise subtracted power spectrum (bottom panel). The processing allow us to extract weak signals as is the case of the first event. These signals correspond to reflection of radio waves from micrometeorites due to their long duration.

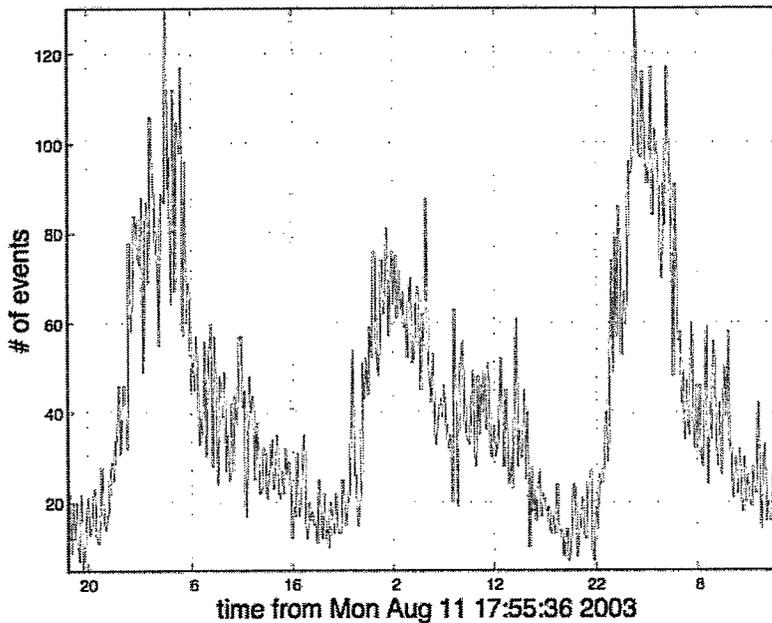


Figure 3. Number of events per 10-minute intervals as function of time of day. The majority of the events happen in the early morning hours when the earth turns into the solar wind.

Generation of Coherent, Femtosecond, High Brightness VUV and X-ray Beams Using High Order Harmonic Conversion

T. Srinivasan-Rao

03-161

PURPOSE:

In recent years there has been significant progress in increasing the brightness of high harmonic generation in the VUV and XUV ranges. In this program we plan to extend the range further to produce high brightness, low divergence photons with energies up to 300 eV and characterize them up to 40 eV (limited by the spectrometer and detector). The program will result in a coherent, fs photon beam with peak brightness of $\sim 10^{13}$ W/(cm² srad) and a photon flux of 10^9 /s over the entire wavelength region. The laser-based high-order harmonic generation source proposed here would be a lab-based source to use as a test bed for ultrafast, soft x-ray experiments and program development during the next few years. If successful, the program will extend the wavelength range for these sources down from the present value of 12 nm to as low as 4 nm, near the carbon K-edge, which is highly valuable for both soft x-ray photochemistry as well as biology. Such a source could act both as a seed for future Free Electron Laser (FEL) development and as a unique test bed ultrafast XUV and soft X-ray techniques for a variety of fields extending from solid state physics and chemistry to structural biology and materials science. The latter could contribute to the scientific case for fourth generation light sources. This advanced study of an innovative concept draws expertise from the Instrumentation Division

and NSLS, which could result in intellectual properties unique to BNL.

APPROACH:

In typical harmonic generation, the energy in the harmonic radiation decreases with increasing order of the harmonic due to the typical Gaussian intensity distribution of the fundamental beam. By modifying the spatial profile of the input beam to that of a first order Bessel function distribution, we plan to generate high harmonic radiation with comparable energy at all harmonics. In addition, by increasing the repetition rate of the gas jet and the laser to kHz, we plan to increase the average flux of the VUV and XUV radiation generated. The project can be subdivided into 4 phases: (1) modification of an existing laser to provide 200 μ J, 10 fs photon pulses at 800 nm with Bessel function intensity distribution, (2) development of high repetition rate gas jets, (3) generation of VUV, XUV radiation up to ~ 100 eV at kHz pulse repetition frequencies (PRF) and its characterization up to ~ 40 eV (limited by the VUV spectrometer and detector at our disposal), and (4) increasing the laser energy to tens of mJ, while maintaining the spatial and temporal characteristics needed for high harmonic generation, at 10 Hz PRF so that shorter wavelength can be generated and characterized in a follow up project.

An existing femtosecond Ti:sapphire laser system is used in this project. The spatial intensity profile of the regenerative amplified laser beam is tailored by sending these femtosecond light pulses through a long hollow capillary tube filled with noble gas to achieve a spatial beam profile with Bessel function distribution. Passage through the noble gas also serves to increase the bandwidth of the input laser and provide a linear chirp that would permit compression

of the pulse duration of the laser. When, this beam interacts nonlinearly with the medium of the gas jet, high quality, low divergence, coherent, ultra short, VUV and soft x-ray beams are generated. The radiation emitted from the gas jet is passed through the entrance slit of a VUV spectrometer onto an iridium-coated grating. The detector is a vacuum photodiode with calibrated phosphor coating to convert VUV radiation to the visible wavelength for detection and characterization. A differential pumping system maintains the gas jet at the required pressure while preserving adequate vacuum in the spectrometer.

TECHNICAL PROGRESS AND RESULTS:

The Ti:sapphire regenerative amplified system consists of a Ti:sapphire oscillator operating at a wavelength of 800 nm, Rep. Rate of 100 MHz with 3 nJ/pulse and 100 fs pulse duration, followed by a regenerative amplifier, resulting in a pulse energy of 0.8 mJ and repetition rate up to 10 kHz. This laser beam is coupled into a high pressure vessel for modifying the spatial profile of the beam.

A pressure vessel (see figure 1 top) capable of supporting 2 atmosphere pressure was constructed to house a 70 cm long hollow, glass, capillary tube of 125 μm in diameter. Figure 1, bottom shows the agreement between the spatial profile of the output beam the calculated Bessel distribution.

Spectral width of the output beam is a key indicator of the shortest pulse duration that can be supported by the laser beam. Hence, increasing the bandwidth of the laser beam is critical to obtaining short laser pulses. As shown in Fig. 2, significant spectral broadening, mostly due to self phase

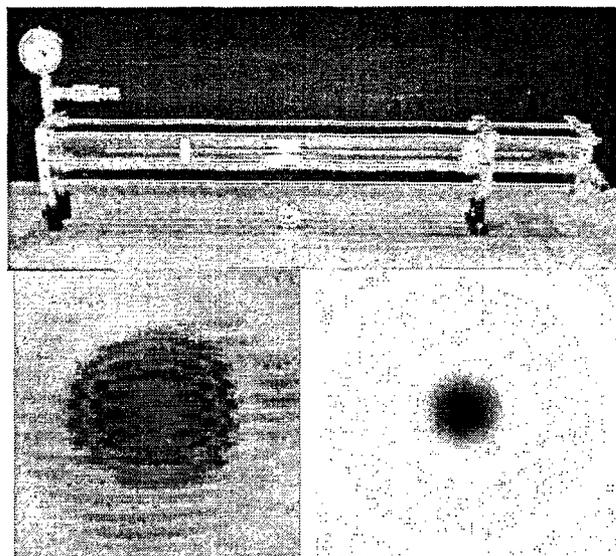


Figure 1. (top) Pressurize housing for the hollow capillary tube. (left) Spatial profile of the output beam after a 70 cm long hollow capillary tube filled with Kr. (right) Calculated beam profile – Bessel function.

modulation, was observed for various noble gases at various pressures. The broadest spectrum, >150 nm, was achieved using Xe (which has the lowest ionization potential of 12.13 eV) gas at 20 psi. Such a large spectral content when compressed appropriately would support a pulse width of ~ 5 femtosecond in duration. Figure 3 shows the linear dependence of the spectral broadening on gas pressure and the length of the hollow capillary tube. It is clear that the longer capillary tube and higher gas pressure is essential on spectral broadening, hence potential for a shorter compress optical pulse. However, the light throughput dropped with increased length of the capillary tube while higher gas pressure promoted more ionization, which further reduces the light throughput. With the present arrangement, more than 25% of light coupling efficiency, 125 μJ of energy/pulse, was obtained in the fundamental wavelength. To increase the light throughput, we intended to coat the internal surface of the longest capillary tube with a

metal film and operate the noble gas at a pressure below the onset of the ionization.

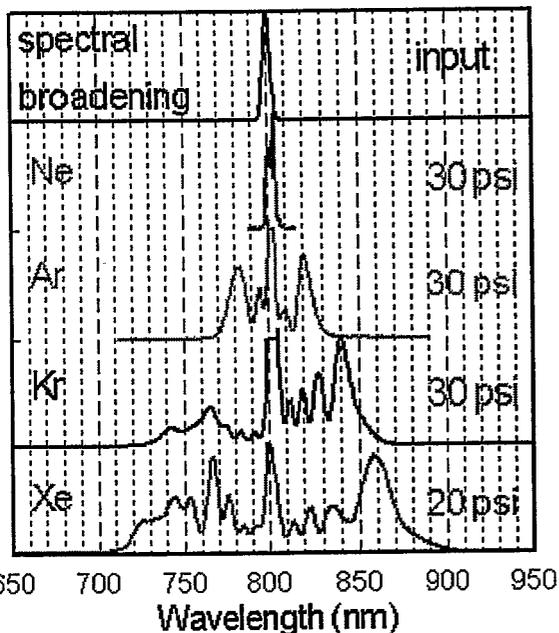


Figure 2. Spectral broadening observed at the output end of the hollow capillary tube that was filled with various noble gases.

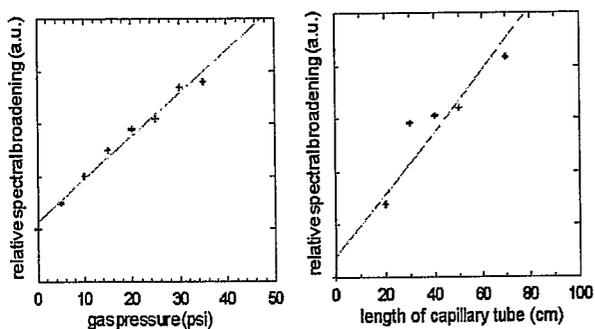


Figure 3. Dependence of the spectral broadening on gas pressures (left) and length of the capillary tubes (right).

A high repetition rate, piezo-driven, pulsed, gas jet has been deigned and is being built. In FY 2004, the uniformity of the gas flow will be characterized using a single-shot laser shadow photograph technique. The compressed high intensity femtosecond light pulse will be irradiated onto the pulsed gas jet that is synchronized to the laser. High harmonic light pulses will then be characterized on a vacuum monochromator. Concurrently, an amplifier system to increase the pulse energy will be designed and constructed.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$130,000 |
| FY 2004 (budgeted) | \$140,000 |

New Synthesis Techniques to Control Atomic Defects in Advanced Intermetallic Compounds

Lance D. Cooley

03-162

PURPOSE:

Advanced intermetallics delicately balance charge, spin and structural energies to create a rich spectrum of correlated electron behavior. In MgB_2 superconductors, for instance, covalent and metallic tendencies combine to produce unique 2-band superconductivity, which survives because interband electron scattering is almost completely prohibited. However, electron scattering is required to make useful upper critical fields, and it is necessary to carefully tune scattering in MgB_2 in order to preserve superconductivity, while also producing desirable properties. New synthesis techniques to manipulate vacancies and alloying elements in advanced intermetallics will be developed by this project.

APPROACH:

MgB_2 is the first material of focus. Considerable effort has been devoted to understanding what defects might occur and what the effects of alloying might be, given that MgB_2 appears to be a stoichiometric line compound. Of chief concern is the possibility of Mg vacancies, due to decomposition of MgB_2 at high temperatures and the volatility of Mg. In this regard, the ability to compose and decompose samples is vital for understanding the binary compound. A special apparatus is being developed to control the Mg vapor pressure independent of the MgB_2 reaction temperature, thereby giving unprecedented control over synthesis. This is being

correlated with studies to decompose MgB_2 *in-situ* using the advanced electron microscopy tools in the Center for Functional Nanomaterials, with the expertise of R. Klie.

Due to the primary contribution of phonons associated with the boron planes, substitution for boron should also produce profound changes in observed properties. However, the high bonding energies makes substitutions at temperatures below ~ 1200 °C sluggish. To drive substitution reactions, additional synthesis routes using boron silicides, carbides, and suboxides will be explored.

TECHNICAL PROGRESS AND RESULTS:

Techniques have been developed to quantify small changes in composition by inductively coupled photoemission (ICP) spectroscopy. This prerequisite study also found that very little variation from stoichiometry exists between samples prepared from a variety of bulk synthesis routes. Although this suggests that Mg and B vacancies are rare, most reaction vessels that have been used can form boride compounds, which may pin compositions at the Mg-rich limit. Thus, it still needs to be clarified whether MgB_2 is indeed a line compound or whether properties change in the B-rich limit.

Re-usable reaction vessels have been developed and these have been used to investigate reactions between Mg and B_6Si , B_4C , and B_6O under identical conditions to understand whether C, O, or Si can be alloyed for B. While no evidence for Si substitution was found, the formation of Mg_2Si appears to accelerate the Mg-B reaction, allowing good superconducting properties to be obtained at reaction temperatures as low as 500 °C. Reactions with B_4C indicated that carbon doping

depends on reaction temperature, which suggests that it may be possible to tune carbon doping of the boron site. However, since carbon also adds electrons, the critical temperature falls quickly with carbon content. Hole doping, such as by alloying the Mg site with lithium, might compensate some of these effects. Studies of oxygen doping have not been concluded.

In FY 2004, the multi-zone heat treatment apparatus will be in operation and will be used to independently control Mg partial pressure during MgB_2 formation. Studies of potential B-site doping will be continued, including using the multi-zone apparatus to selectively dope the Mg site with Li. Further work on oxygen and aluminum doping is also planned.

As the techniques for synthesis are improved, new experiments may probe other intermetallics that have similar synthesis challenges as MgB_2 . This may include the

potential overlap of ferromagnetism and superconductivity in $MgCNi_3$, giant magnetocaloric effects in Mn_3GaC and perhaps other materials where the volatile element chemistry is crucial and where covalent tendencies play a role.

SPECIFIC ACCOMPLISHMENTS:

L. D. Cooley, V. Solovyov, and H. Wiesmann, "Analysis of Mg:B stoichiometry by inductively coupled photoemission spectroscopy," (in preparation).

L. D. Cooley, A. Moodenbaugh, and R. F. Klie, "Low-temperature synthesis of MgB_2 from B_6Si ," (in preparation).

LDRD FUNDING:

| | |
|--------------------|-----------|
| FY 2003 | \$ 88,000 |
| FY 2004 (budgeted) | \$144,000 |

Appendix A

2004 Project Summaries

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: February 7, 2003
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. Proposals must be submitted by April 2, 2003, through the respective Chairperson and the Associate Laboratory Director to the Administrator for LDRD (Kevin Fox in Bldg. 460). Electronic versions of the Proposal Information Questionnaire submission form can be obtained by going to <https://sbms.bnl.gov/standard/3c/3c02e011.htm> or from greco@bnl.gov. The BNL LDRD Policy, which defines the LDRD Program, can be reviewed at this web site. 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 we require an abstract to fit on the first page of the form and a proposal which is not more than three pages in length. Also, note that LDRD projects are restricted to a maximum of three years. However, projects should be tailored to a two-year schedule. Along with your proposal you are requested to include a milestone schedule of activities to be completed with planned accomplishments and dates of completion of for example: lab setups, test runs or trials, compiled data sets, reports to be issued on results, etc. In addition, this year we are requesting a one-page vita. In each year there is a mid-year review of all programs to assess the extent of progress.

Research conducted under LDRD should be highly innovative, and an element of high risk as to success is acceptable. This year we will be especially pleased to receive proposals in the areas of advances in computational sciences, materials sciences, and biotechnology. Over the years the budget allocation has been increased to \$8.5 million, and as a consequence we should have approximately two to three million dollars for new starts.

The Selection Committee will be chaired by the Scientific Director for LDRD and includes the Director for Science and Technology along with the Associate Laboratory Directors and is augmented by selected distinguished scientists. The committee starts meeting in April to evaluate proposals for selection for funding in FY 2004.

For your convenience and planning purposes, note the following calendar for LDRD activities and the attached copy of the new Proposal Information Questionnaire.

| | |
|------------------------|--|
| February 7, 2003 | Call for FY 2004 Proposals |
| April 2, 2003 | FY 2004 Proposals Due |
| April 1-3, 2003 | FY 2003 Mid-Year review |
| April 28 –May 31, 2003 | Selection of FY 2004 LDRDs |
| August 15, 2003 | FY 2004 Plan Due to DOE |
| October 1, 2003 | Funding of FY 2004 Projects |
| October 10, 2003 | Call for FY 2003 Annual Reports |
| November 13, 2003 | Annual Reports Due on FY 2003 Projects |

LN:kjf
Attachments

Distribution:

Associate Laboratory Directors
Department Chairpersons

cc: G. Fess
K. Fox
W. Hempfling
D. Johnson
N. Narain
P. Paul
Assistant Laboratory Directors
Division Managers

Exhibit B

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 (month/year) From _____ Through _____

SUMMARY OF PROPOSAL

Description of Project:

Expected Results:

INSTRUCTIONS

Under **Description of Project**, provide a summary of the scientific concept of the proposed project including the motivation for the undertaking and the approach that will be used to conduct the investigation. Also indicate how the project meets the general characteristics of the LDRD Program and how it is tied to the DOE Mission. Under **Expected Results**, clearly enunciate what are the expected results and how they will impact the science. These items should not exceed the space remaining on this page, using the given font and size. Follow this page with an extended Proposal of no more than three (3) pages in length plus a Milestone Schedule. In addition, include a one-page Vita of the Principal Investigator; fill out the page with citations to recent pertinent publications. Do not include any additional attachments, as these will be discarded. Complete the Questionnaire, obtain the required approvals, and provide a Budget in the format on the form supplied. 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, postdoctoral research associates, and/or students. Identify the various burdens applied, i.e., organizational, materials, and contracts. Include any other charges but the Laboratory G&A should not be applied. Go to the LDRD web site (www.bnl.gov/ldrdr/) for further information. **(This paragraph should be deleted before you input the requested information.)**

PROPOSAL

VITA (Principal Investigator)

LDRD MILESTONE SCHEDULE

| Date | Planned Accomplishments |
|-----------|-------------------------|
| 6 months | |
| 1 year | |
| 18 months | |
| 2 years | |
| 30 months | |
| 3 years | |

1. 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 _____

2. VERTEBRATE ANIMALS

Are vertebrate animals involved?
If **yes**, has approval from BNL's Animal Care and Use Committee been obtained?

Y/N _____

Y/N _____

3. 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.)

4. 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 _____

Are biohazards involved in the proposed work? If yes, attach a current copy of approval from the Institutional Biosafety Committee.

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, etc.) in which it will be performed?

Y/N _____

If **no**, attach a statement indicating what has to be done and how modifications will be funded to prepare the facility to accept the work.

5. TYPE OF WORK

Basic/Applied _____

6. CATEGORY OF WORK (select one by placing an X)

| | | | |
|--|-------|---------------------------------------|-------|
| Advanced Sensors & Instrumentation | _____ | Engineering & Manufacturing Processes | _____ |
| Biological Sciences (including medical) | _____ | Materials Science and Technology | _____ |
| Chemistry | _____ | Mathematics and Computing Sciences | _____ |
| Earth and Space Sciences (including environmental) | _____ | Nuclear Science and Engineering | _____ |
| Energy Supply and Use | _____ | Physics | _____ |

7. 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 _____

| | |
|------------|-----------|
| Print Name | Signature |
|------------|-----------|

Department Chair/Division Manager _____

| | |
|------------|-----------|
| Print Name | Signature |
|------------|-----------|

Cognizant Associate Director _____

| | |
|------------|-----------|
| Print Name | Signature |
|------------|-----------|

BUDGET REQUEST BY FISCAL YEAR

(Note: Funding for more than 2 years is unlikely and 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 ITD Charge Other (specify) | | | |
| TOTAL PROJECT COST | | | |
| * Labor (indicate names, type of staff and level of effort, and where names are not known indicate TBD) | | | |
| List all materials costing over \$5000 | | | |

Exhibit C

LDRD DATA COLLECTION FORM

Read and then remove the instructions before attempting to complete this form and return it electronically to D. J. Greco (greco@bnl.gov)

LDRD PROJECT NUMBER:

PROJECT TITLE:

PRINCIPAL INVESTIGATOR(S):

PUBLICATIONS

TOTAL _____

List all refereed publications originating in whole or in part from this LDRD including those that have been submitted, but do not include any that are in preparation. Provide the total number above.

Example of style

Ozone production in the New York City Urban Plume. Kleinman, L. I., Daum, P. H., Imre, D. G., Lee, J. H., Lee, Y. -N., Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., and Newman, L. J. *Geophys. Res.*, 105, 14,495-14,511 (2000).

MEETINGS, PROCEEDINGS, AND ABSTRACTS

TOTAL _____

List all formal presentations originating in whole or in part from this LDRD including those that have been accepted for presentation but not yet presented. Provide the total number above.

Example of style

Ozone production in the New York City urban plume. Kleinman, L., Daum, P. H., Imre, D., Klotz, P., Lee, J. H., Lee, Y. N., Nunnermacker, L. J., Springston, S., Weinstein-Lloyd, J., and Newman, L. American Geophysical Union Fall Meeting, San Francisco, CA, Dec. 8-12, 1997.

REPORTS

TOTAL _____

List all formal reports originating in whole or in part from this LDRD including those that have been accepted for publication, but do not include any that are in preparation. Provide the total number above.

PATENTS AND LICENSES

TOTAL _____

List all patents and licenses originating in whole or in part from this LDRD including those that are pending, but not any that are in preparation. Provide the total number above.

COPYRIGHTS**TOTAL _____**

List all copyrights (other than publications) originating in whole or in part from this LDRD including those that are pending, but not any that are in preparation. Provide the total number above.

INVENTION DISCLOSURES**TOTAL _____**

List all invention disclosures submitted to the Laboratory's Office of Intellectual Property & Sponsored Research that were either directly derived from this LDRD or from any follow-on efforts. Provide the total number above.

PROJECT REVIEWS**TOTAL _____**

List all formal review presentations that pertain to this work. Include the name of the reviewing body and date of review, title of presentation, and names of presenters. Do not include the mid-year LDRD program reviews. Provide the total number above.

STUDENTS AND RESEARCH ASSOCIATES**TOTAL _____**

Provide names of all graduate students and Research Associates supported during the duration of this LDRD and give the number of months that they were supported. Provide the total number above combined as full-time equivalents, rounded to the nearest month.

NEW HIRES**TOTAL _____**

Provide names of any new staff that were hired as a direct result of this LDRD. Provide the total number above.

FOLLOW-ON FUNDING**TOTAL _____**

List all requests for funding including any that have been rejected, and those still pending decisions but not any that are in preparation. Give the title of the project, the Principal Investigator, date of submission, the name of the agency, action taken, amount funded or requested per year, and the duration. Provide the total number above.

AWARDS**TOTAL _____**

Provide information on any national awards or recognitions received that are attributable in whole or in part to LDRD projects funded in any year. For each award, describe (in 150 words or less) its significance and the role that LDRD played in achieving it. Provide the total number above.