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Brookhaven National Laboratory's

Annual Report of

Laboratory Directed Research & Development Program Activities For FY 2004

Director's Office

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
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Acknowledgments

The Laboratory Directed Research and Development (LDRD) Program is managed by Leonard Newman, who serves as the Scientific Director, and by Kevin Fox, Special Assistant to the Assistant Laboratory Director for Finance (ALDF). Preparation of the FY 2004 report was coordinated and edited by Leonard Newman and Kevin Fox, who wish to thank D.J. Greco, Regina Paquette, and Maria Ohlsen for their assistance in organizing, typing, and proofing the document. A special thank you is also extended to the Photography and Graphic Arts Group for their help in publishing. Of course, a very special acknowledgement is extended to all of the authors of the project annual reports and to their assistants.

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Introduction

Brookhaven National (BNL) Laboratory is a multidisciplinary laboratory that carries out basic and applied research in the physical, biomedical, and environmental sciences, and in selected energy technologies. It is managed by Brookhaven Science Associates, LLC, under contract with the U. S. Department of Energy. BNL's total annual budget has averaged about $460 million. There are about 2,800 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 2004. 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 2004 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 2005. The BNL LDRD budget authority by DOE in FY 2004 was $9.5 million. The actual allocation totaled $8.5 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 and Self Assessment.

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 Site Office 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 2004, the Program Committee--which selected the 2005 programs--consisted of eleven 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.

2004 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)**
Steven Dierker	**Light Sources (ALD)**
Doon Gibbs	**Basic Energy Sciences (ALD)**
Walter Mangel	**Biology (S)**
George Hendrey	**Environmental Sciences (S)**
Benjamin Ocko	**Physics (S)**
Grahm Smith	**Instrumentation (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 was historically 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 significantly 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%.

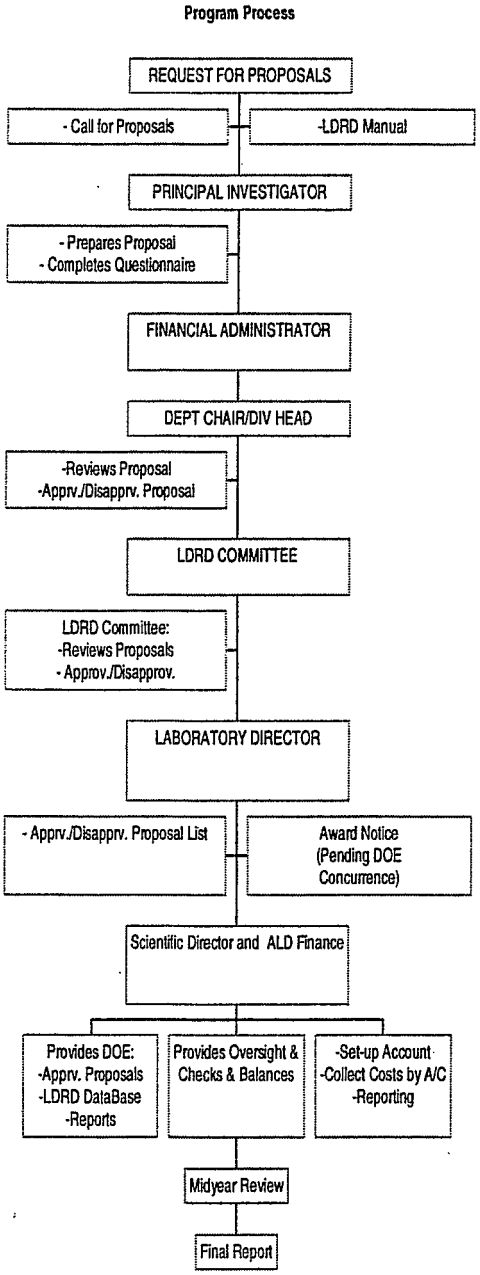
Request for Proposals: The availability of special funds for research under the LDRD Program is well publicized throughout the Laboratory. This is done using two methods -- one occurring at yearly intervals, the other occurring irregularly. Each year a call letter is sent by the SD for LDRD to the Scientific Staff and as a separate memorandum to all the Associate Laboratory Directors and Department Chairpersons. The FY 2005 call issued in February 2004 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. The DOE Project Manager is present during the Committee evaluation sessions as a non-voting member.

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 create a commitment of future multi-year funding to reach a useful stage of completion; and (8) 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 Site Office (DOE-BHSO) for concurrence by the DOE Project Manager 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 is the SD, the DDS&T, the cognizant ALD and Department Chair, and a representative from the ALDF and DOE-BHSO. 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-BHSO 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 data 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://ldrdrpt.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.

All projects selected for approval are reviewed by the BNL Operations Security (OPSEC) Working Committee chair for classification review and operational security considerations.

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 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 2004, BNL did a complete formal new 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 for those that responded they gave a neutral review of the administration of the LDRD Program. The scoring for each category of questions fell between Tend to Agree and the Tend to Disagree rating. The highest rating was noted for response to whether the Scientific Director and LDRD Staff foster open communication and spirit of cooperation. As a result of the Self Assessment survey and Laboratory Management interest in improving the LDRD program, the Laboratory conducted an additional Self Assessment of the LDRD selection process. After concluding, the FY04 team representing the ALD and Laboratory management was convened to review the selection process and implemented changes. The process changes included limiting final selection for all Lab-wide competition LDRD projects to the ALDs, also creating a Director's Strategic Reserve to address off- cycle Laboratory needs.

In addition, the LDRD Office is now attending monthly meetings with the Integrated Planning Office to coordinate efforts of strategic planning for the Laboratory. These changes have been incorporated in the LDRD SBMS subject .

The FY 2005 LDRD Plan was submitted to DOE in August of 2004 for review. The plan included reference to these self-assessment changes to the program. In October of 2004 the 2005 Plan was approved by DOE-BHSO and DOE-HQ.

The FY 2004 changes to the program were a result of the SD of the LDRD and ALDF staff being knowledgeable and responsive to changes prompted by customer inquiries.

Summary of Additional Opportunities for Improvements:

The areas identified below as opportunities for improvement will only enhance current operations and foster continuous improvement of the LDRD process at Brookhaven. 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 Laboratory's overall Strategic Plan.

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
- Porphryin 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 • RHIC • NSLS • ATF • LEAF • STEM • Tandem • BMRR	**0**
2	Nuclear Physics • Quark/gluon plasma • Spin Physics	**1**
3	High Energy Physics • Standard Model • Rare Particles & Processes	**2**
4	Advanced Accelerator & Detector Concept and Designs - Advanced Instrumentation • Muon Collider • DUV-FEL • LHC • SNS	**12**
5	The Physics & Chemistry of Materials • Superconductivity • Magnetism • Surfaces • Nanostructure	**12**
6	Energy Sciences • Combustion • Catalysis • Bio-fuels • Batteries • Geothermal • Buildings	**9**
7	Environmental Sciences • Atmospheric • Terrestrial • Bio-remedial • Waste Technologies • Counter Terrorism	**16**
8	Medical and Imaging Sciences & Technology	**9**
9	Advanced Computation	**0**
10	Biological Sciences	**10**
11	Critical Infrastructure	**1**
Totals		**72**

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 2004 LDRD Program. The LDRD Program at BNL is expanding and is generating interest from across the entire Laboratory population.

In FY 2004, the BNL LDRD Program funded 72 projects, 19 of which were new starts, at a total cost of $7,208,543. Included in this report is the Project Funding Table, which lists all of the FY 2004 funded projects and gives a history of funding for each by year.

FY	DOE AUTH. $K	BNL AUTH. $K	COSTED $K	NO. RECD.	NEW STARTS	TOTAL FUNDED
1985	4,000	1,842	1,819	39	13	13
1986	4,500	2,552	2,515	22	15	25
1987	4,000	1,451	1,443	29	8	17
1988	4,000	1,545	1,510	46	14	23
1989	4,000	2,676	2,666	42	21	29
1990	4,000	2,008	1,941	47	9	26
1991	2,000	1,353	1,321	23	14	21
1992	2,500	1,892	1,865	30	14	25
1993	2,500	2,073	2,006	35	14	28
1994	2,500	2,334	2,323	44	15	27
1995	2,500	2,486	2,478	46	13	31
1996	3,500	3,500	3,050	47	17	31
1997	4,500	4,500	3,459	71	10	28
1998	3,500	4,000	2,564	53	4	20
1999	4,750	4,612	4,526	67	25	33
2000	6,000	6,000	5,534	93	21	45
2001	6,000	6,000	5,345	97	38	70
2002	7,000	7,000	6,732	87	29	70
2003	8,500	8,482	7,830	153	44	83
2004	9,500	8,550	7,209	107	19	72
2005	10,500	9,073		114	41	78
TOTALS	100,250	83,929	68,136	1,292	398	795

An analysis of the FY 2004 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 2004 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.	134
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.	231
Total number of reports originating in whole or in part from this LDRD.	21
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.	4
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.	11
Total number of review presentations that pertain to this work.	19
Total number of students and postdocs (combined total as FTEs) directly supported by this LDRD project while this project was active.	53
Total number of new, permanent, full-time staff hired as a direct result of this LDRD Project.	23
Total number of proposals submitted for follow-on funding (other than LDRD).	95
Total number of national awards or recognitions received that are attributable in whole or in part from this LDRD.	10

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

In conclusion, the overall LDRD Program has been successful. In FY 2004, the LDRD Program has improved on the level established in FY 2003 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 2004 the Laboratory continued to experience a significant scientific gain by the achievements of the LDRD Projects.

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2004

LDRD Proj. No.	Project Title	P.I.	Dept./Bldg.	Theme	Actual FY 02$	Actual FY 03 $	Actual FY04 $	Approved FY05	Requested FY06 $	Total
02-02	Crystallization and X-ray Analysis of Membrane Proteins	Fu, D.	BIO/463	10	380,454	396,551	410,554			1,187,559
02-08	Creating a MicroMRI Facility for Research and Development	Benveniste, H.	MED/490	4	94,494	193,613	178,948			467,055
02-09	Targeting Tin-117m to Estrogen Receptors for Breast Cancer Therapy	Kolsky, K.	MED/801	10	48,242	98,671	49,009			195,922
02-22	Electrical Systems Reliability	Bari, R.	ES&T/475B	11	83,965	99,081	103,512			286,558
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	100,000	149,232			348,452
02-70	Theory of Electronic Transport in Nanostructures and Low-Dimensional Systems	Tsvelik, A.	CMP/510A	5	134,268	115,000	148,483			397,751
02-71	Pressure in Nanopores	Vogt, T.	CMP/510A	5	79,000	82,600	57,423			219,023
02-84a	Genomic SELEX to Study Protein DNA/RNA Interactions in *Ralstonia metallidurans* CH34 Regulating Heavy Metal Homeostasis and Resistance	van der Lelie, D.	BIO/463	10	163,972	170,900	161,662			496,534
02-84b	Lead Resistance in *Ralstonia metallidurans* CH34	Taghavi, S.	BIO/463	10	161,408	170,100	169,708			501,216
02-86	Ultrafast X-Ray Science	Dierker, S.	NSLS/725B	5	100,018	105,000	104,578			309,596
02-88	X-Ray Photon Correlation Spectroscopy Studies of Nanostructured Block Copolymers	Dierker, S.	NSLS/725B	5	90,212	105,000	104,775			299,987
03-004	High-Brightness, High-Power Electron Beams	Ben-Zvi, I.	CAD/817	4		150,000	192,464	190,000		532,464
03-006	Feasibility Study of Optical Stochastic Cooling with a CO2 Laser	Yakimenko, V.	PHYS/820M	4		110,000	121,834			231,834
03-013	Proposal for Niobium/Tin Superconducting Magnet	Willen, E.	SMD/902A	4		147,800	156,269			304,069

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2004

03-014	Technology Development for Linear Collider Final Focus Quadrupoles with Small-Aperture High-Gradient Superconducting Coils	Parker, B.	SMD/902A	4		125,000	129,829			254,829
03-026	Developing a New, Unified Systems Theory on Size Distributions of Atmospheric Particles	Liu, Y.	ESD/815E	7		45,000	45,447			90,447
03-027	Measurement of HO2 Radicals by ChemiLuminescence Analysis of Atmospheric Radicals (CLAAR)	Springston, S.	ESD/815E	7		100,000	99,045			199,045
03-030	Chemistry of the Rhizosphere	Fuhrmann, M.	ESD/830	10		100,000	101,573			201,573
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		66,000	67,283			133,283
03-050	Evaluation of High-Energy Radiation Effects in Materials	Greene, G.	ES&T/703	5		100,000	105,354			205,354
03-056	Structural Properties of Methane Hydrates	Mahajan, D.	ES&T/815	6		85,000	103,647	15,000		203,647
03-061	Dynamics of Wind Turbine-Tower-Foundation Systems	Philippacopoulos, A.	ES&T/526	6		140,000	145,957			285,957
03-064	Investigation of Neutron and Gamma Probes to Detect Explosives in Sealed Containers	Todosow, M.	ES&T/475B	7		110,000	112,370	92,000		314,370
03-065	Ultrasound and Infrared Imaging to Detect Degradation of Electric Cable Insulation	Villaran, M.	ES&T/130	6		63,000	74,604			137,604
03-072	Application of Compton-Suppression Gamma-Ray Spectrometry to Counterterrorism Problems	Lemley, J.	NNS/197C	7		125,000	134,174			259,174
03-077	Real-Time Consequence Assessment System for Atmospheric Terrorist Events in the Northeast Urban Corridor	Reynolds, R.M.	ESD/490D	7		70,000	72,951			142,951
03-081	Application of Thin Film-Like Dosimeters for Port Security and Anti-Terrorism	Kaplan, E.	NNS/197C	7		110,000	100,696			210,696

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2004

03-083	Novel Xenon Detector Concepts for Homeland Defense	Vanier, P.	NNS/197C	7		100,000	103,976			203,976
03-086	Defining New Pathways for Disarming Anthrax Toxin	Freimuth, P.	BIO/463	7		100,000	99,543			199,543
03-094	Structural Studies on the Integral Membrane Protein AlkB	Shanklin, J.	BIO/463	10		55,000	96,692	40,000		191,692
03-098	Roles of Dopamine Receptor Agonists in Brain Metastasis of Breast Cancer	Lin, X.	MED/490	8		100,000	99,091			199,091
03-099	The microPET Study of Gene Expression in Rodents	Thanos, P.	MED/490	8		50,000	94,700	50,000		194,700
03-100	Investigation of the "Early Response" in Functional MRI	Ernst, T.	MED/490	8		240,000	123,500			363,500
03-101	PET Imaging of Violent Behavior	Wang, G.-J.	MED/490	8		100,000	98,978			198,978
03-103	PET Study of Acetaldehyde Distribution and Metabolism to Better Understand Alcohol Related Diseases	Benveniste, H. for Li, Zizhong	MED/490	8		100,000	98,889			198,889
03-104	Hydrogen Atom Transfer from Carbon to Metal - Relevance of a Novel Reaction to Catalyzed Hydrocarbon Conversions	Bullock, M.	CHEM/555A	6		20,000	56,480	58,000		134,480
03-105	Radioprotection in D. Radiodurans, a Radiation Resistant Bacterium	Cabelli, D.	CHEM/555A	10		57,500	74,668	17,500		149,668
03-107	New Development of Norepinephrine Transporter Radioligands for PET Studies of Substance Abuse, Depression and ADHD	Ding, Y.-S.	CHEM/555A	8		112,000	111,095	93,000		316,095
03-108	Experiments in the Short-Wavelength Regime Pertinent to the DUV-FEL Concept	DiMauro, L.	CHEM/555A	4		132,000	131,367			263,367
03-115	Imaging Tandem Mass Spectrometry for High-Throughput "Fingerprint" Detection of Complex Molecules in Mixtures	Suits, A.	CHEM/555A	7		113,000	109,593			222,593
03-118	Condition: Green Chemistry Radiolytic Studies of Ionic Liquids in Service of Security and the Environment	Wishart, J.	CHEM/555A	7		43,000	79,517	37,000		159,517
03-119	Exploring the Use of Powder Diffraction for Proteins	Allaire, M.	NSLS/725D	10		45,000	79,445	35,000		159,445

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2004

03-121	Element-Resolved Dynamics of Nanoscale Ferromagnets	Kao, C.-C.	NSLS/725D	5		30,000	79,558	50,000		159,558
03-122	Membrane Biophysics Using Model Membranes	Pindak, R.	NSLS/725D	10		30,000	79,316	50,000		159,316
03-127	High Pressure in Strongly Correlated Materials - An Optical Investigation	Homes, C.	CMP/510B	5		54,400	66,865	11,000		132,265
03-129	Polyoxometalate Giant Molecules: Novel Synthetic Methods, Characterizations and Potential Applications	Liu, Tianbo	CMP/510B	6		54,000	95,532	46,000		195,532
03-135	Exploratory Sol-Gel Synthesis	Vogt, T.	CMP/510B	5		75,000	81,047			156,047
03-137	In Situ Soft X-Ray Absorption Spectroscopy Studies of Cathode Materials for Thin Film Lithium-Ion Batteries	Yoon, Won-Sub for Balasubramanian, M.	MSD/555	6		80,000	46,337			126,337
03-138	Functional Bulk Mn-Based Nanocomposites	Lewis, L.	MSD/480	5		28,000	76,906	42,000		146,906
03-144	Nanostructured Transition Metal Oxides	Wu, L.	MSD/480	5		40,000	76,347			116,347
03-151	Radio Wave Detection of Ultra High Energy Cosmic Rays	Takai, H.	PHYS/510A	3		100,000	123,923	25,000		248,923
03-161	Generation of Coherent, Femtosecond, High Brightness VUV and X-Ray Beams Using High Order Harmonic Conversion	Srinivasan-Rao, T.	INST/535B	4		130,000	139,719			269,719
03-162	New Synthesis Techniques to Control Atomic Defects in Advanced Intermetallic Compounds	Cooley, L.	MSD/480	5		88,000	90,577	71,000		249,577
04-011	Femtosecond Photoinitiated Nanoparticle Surface Chemistry	Camillone, N.	CHEM/555	6			79,532	121,000	41,000	241,532
04-013	Chirped Pulse Amplification at the DUV-FEL	Yu, L.H.	NSLS/725C	4			78,404	120,000	41,000	239,404
04-025	Overcoming Coherent Instabilities at Medium-Energy Storage Rings	Wang, J.-M.	NSLS/725C	4			91,415	140,000	48,000	279,415
04-033	Layered Cobaltates with High Thermoelectric Power	Li, Qiang	MSD/480	6			61,780	101,000	32,300	195,080
04-041	Lattice QCD Relevant for RHIC and AGS	Petreczky, P.	PHYS/510A	2			69,272	108,000	37,000	214,272
04-043	Very Long Baseline Neutrino Oscillation Experiment	Diwan, M.	PHYS/510E	3			71,099	106,000	36,000	213,099

FUNDING TABLE OF LDRD PROJECTS APPROVED FY 2004

04-046	Advanced 3He Detectors for the Spallation Neutron Source	Smith, G.	INST/535B	4			72,953	110,000	37,400	220,353
04-055	Genetic NanoTags	Hainfeld, J.	BIO/463	5			12,933	115,000	99,000	226,933
04-060	The Use of Singular Point Genome Sequence Tags to Analyze Community Composition and Metabolic Potential	van der Lelie, D.	BIO/463	10			121,236	188,000	63,000	372,236
04-061	3-D Electronic Wave Functions from EM Images	Wall, J.	CFN/463	4			98,945	150,000	51,000	299,945
04-062	Functional MRI Studies in Rats using Implanted Brain Electrodes	Gifford, A.	MED/490	8			78,466	120,000	41,000	239,466
04-063	Optimizing Functional Neuroimaging Techniques to Study Brain Function in Health and Disease States	Goldstein, R.	MED/490	8			100,684	150,000	51,000	301,684
04-066	Technological Development of a Fluorescence Probe for Optical Detection of Brain Functional Activation *in vivo*	Du, C.	MED/490	8			27,032	130,000	104,000	261,032
04-069	Nuclear Control Room Unfiltered Air In-Leakage by Atmospheric Tracer Depletion (ATD)	Dietz, R.	ESD/815E	7			59,463	90,000	31,000	180,463
04-073	Perfluorocarbon Tracer Sampling, Tagging and Monitoring Techniques for use at the Urban Atmospheric Observatory	Heiser, J.	ESD/830	7			65,530	100,000	34,000	199,530
04-079	Development of an Aerosol Mobility Size Spectrometer and an Aerosol Hygroscopicity Spectrometer	Wang, J.	ESD/815E	7			65,589	100,000	34,000	199,589
04-086	Exploration of Thermal Diffusion Processes in CdZnTe for Improved Nuclear Radiation Detectors	Bolotnikov, A.	NNS/197C	7			86,077	130,000	44,000	260,077
04-088	An Integrated Approach of High Power Target concept Validation for Accelerator-Driven Systems	Simos, N.	ES&T/475B	4			82,747	125,000	43,000	250,747
04-104	Hydrogen Storage Using Complex Metal Hydrides for Fuel Cell Vehicles	Wegrzyn, J.	ES&T/815	6			70,265	110,000	37,000	217,265
	TOTALS:				$1,435,253	$5,360,216	$7,208,543	$3,435,500	$1,211,700	$18,651,212

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2004 PROJECT PROGRAM SUMMARIES

Crystallization and X-ray Analysis of Membrane Proteins

Dax 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 Laboratory Directed Research & Development (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:

We have met all the planned milestones at the end of 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 extended x-ray absorption fine structure (EXAFS) and ^{113}Cd nuclear magnetic

resonance (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 have met most milestones for FY 2004. Hundreds of YiiP crystals were produced under a dozen of additive conditions. We initiated crystal screening on beam line X25 at the National Synchrotron Light Source (NSLS) and identified several diffracting crystals that can diffract to 3-4 Å range. Heavy metal ions were present in the crystallization setup, thus eliminating the need for making heavy atom derivatives by crystal soaking or selenium-Met expression. A complete dataset to 6.2 Å was collected, which allowed initial assignment of the space group. At this resolution, we are not able to solve the YiiP structure, but this preliminary result warrants further improvement toward high-resolution diffraction.

SPECIFIC ACCOMPLISHMENTS:

Four papers were published in 2004. In addition, two more papers are in preparation and several projects are making rapid progresses.

Chao, Y. and Fu, D. Kinetic study of the antiport mechanism of an *Escherichia coli* zinc transporter, ZitB. J. Biol. Chem. 279(13), 12043-12050 (2004).

Chao, Y. and Fu, D. Thermodynamic studies of the mechanism of metal binding to the *Escherichia coli* zinc transporter YiiP. J. Biol. Chem. 279(17), 17173-17180 (2004).

Daniels, B. V., Jiang, J.-S., and Fu, D. Crystallization and preliminary crystallographic analysis of the *Escherichia coli* water channel AqpZ. Acta Crystallographica Section D: Biological Crystallography D60, 561-563 (2004).

Wei, Y., Li, H., and Fu, D. Oligomeric state of the *Escherichia coli* metal transporter YiiP. J. Biol. Chem. 279(38), 39251-39259 (2004).

Preliminary studies with metal transporters allowed us to submit a RO1 grant to NIH in 2004. These results are not reports of pre-FY 2004 work.

LDRD FUNDING:

FY 2002	$380,454
FY 2003	$396,551
FY 2004	$410,554

Creating a MicroMRI Facility for Research and Development

Helene Benveniste *02-008*

PURPOSE:

To determine the feasibility and then 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 SBU investigators whose research requires functional and high-resolution anatomical imaging of small animals, plants, or other bioorganisms.

APPROACH:

The ability to characterize genotype-phenotype relationships in genetically engineered small animals is extremely important for understanding the role of specific genes in normal and pathological processes pertaining to biological life at all levels. – The 9.4T microMRI facility will enable phenotyping of transgenic small animals at several biological levels: microanatomical (30-100 micron cubic resolution), physiological, functional and biochemical (spectroscopy).

TECHNICAL PROGRESS AND RESULTS:

FY03 Progress: The 9.4T instrument arrived in September 2003 and was brought up to field by Magnex engineers in two phases due to a minor misalignment of the inner core of the magnet. The corrections were made and the 9.4T is currently up to its field of 9.4T and meets all instrument specifications and sensitivities. Bruker BioSpin software engineers spent time with BNL MR physicists and bioengineers to train in use of the Paravision software that controls the MR instrument. The training was completed in January 2004.

The following technical progress has been successfully implemented:

Scan synchronous ventilation & and cardiac gating during image acquisitions on rats and 30-g mice

0.0078 mm3 spatial resolution in MR microscopy images of the C57BL6/J mouse brain in vivo

Quantitation of cerebro-spinal fluid flow in rat brain

SPECIFIC ACCOMPLISHMENTS:

Current 9.4T microMRI projects

Project Title	PIs	Funding
In vivo tracking of human stem cell by MRS	Maletic-Savatic Rooney Benveniste	PSTA to Dr. Maletic-Savatic $150,000/yr
In vivo tracking of medically loaded magnetic nanopowders, and ceramic nanocomposites in rodents using microMRI	Tsalakakos … Benveniste Rooney	NIH grant to be submitted Feb. 1 Pilot project
C57BL6/J Mouse brain atlas by MR microscopy	Benveniste Blackband Hof	NIBIB (ends June 2004)
Detection of lesions in an EAE rat model of Multiple sclerosis	Pena, Rooney, Fang, Li	DOE
Brain morphological changes after early-onset seizures in Rats	O'Neill, Rooney Benveniste	Pilot project

Optical fluorescence based recording of calcium transients during functional activation in the rat brain combined with fMRI based BOLD signal changes.	Du, Benveniste	DOE MO-065 LDRD
fMRI studies in rat brain with implanted electrodes	Gifford, Du, Benveniste, Luo	LDRD
CSF flow in rats with hydrocephalus	Wagshul	Pilot project
Brain volumetric studies of Dopamine-2 knockout mice exposed to alcohol	Benveniste, Thanos	Pilot ADHD network

LDRD FUNDING:

FY 2002	$ 94,494
FY 2003	$193,613
FY 2004	$178,948

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.

While this was the original purpose of this project, several developments necessitated a change in direction. For 2004 we proposed to synthesize a different steroid hormone radioligand, 11-methoxy-16-alpha estradiol, which has not previously been radiolabeled with iodine, and label it with I-123 for Auger electron studies (for cancer therapy applications) and I-124 for Positron Emission Tomography (PET) studies (for imaging applications). This work would allow our group to collaborate with a new scientist in the Medical Department, Anat Biegon, who is also interested in steroid radioligands for measuring occupancy of brain estrogen receptors by anti-cancer drugs. The ligand molecule synthesized in this project could be used for both projects, depending on the radioisotope attached to the molecule.

In FY 2004, we proposed 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, 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.

However, several developments 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.

A third development arose in June of 2003 when the research associate working on this project, Dmitry Kosynkin, accepted an appointment within the Chemistry Department at BNL.

It was 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 Ding, within the PET group of the Chemistry Department, and nuclear and radiolabeling chemists, myself and Dr. Benat 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 accomplished by colleagues of Dr. Benat'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.

The synthetic organic work proved to be more technically difficult than originally anticipated. The synthesis of proposed molecule, 11-beta-methoxy-16-alpha-iodo-17-beta-estradiol, could not be duplicated given the published procedure and was therefore attempted as a new synthesis. This synthesis was approximately 50% complete upon termination of this project.

SPECIFIC ACCOMPLISHMENTS:

To support the radiolabeling efforts of this project, an IPP Thrust 2 project was written and funded to develop a source of no-carrier-added Sn-117m radionuclide. In addition, a source for Sn-113, a long-lived stand-in for Sn–117m was developed with Los Alamos National Laboratory. Sn-113 will be used in place of Sn-117m until its production method has been developed.

LDRD FUNDING:

FY 2002	$ 48,242
FY 2003	$ 98,671
FY 2004	$ 49,009

Electrical Systems Reliability

Robert A. Bari *02-022*

PURPOSE:

The purpose of this project is 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 have been working collaboratively with Con Edison including the first pilot application of this methodology. 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.

An integral part of this methodology is the capability to simulate the grid response for multiple contingencies under various configurations. A time-dependent computer simulation model with sufficient flexibility to analyze a range of security problems was developed. Our strategies to address the challenges to power grids consist of network design improvements, hardware redesign, improvements or additions to monitoring capabilities, software redesign, and operating procedure revisions.

TECHNICAL PROGRESS AND RESULTS:

Various tools and methods have been developed to evaluate the grid reliability together with a deterministic methodology for several decades. Most of the developed tools either do not have open source codes that can be tailored for a specific research topic or a multiple-purposed integrated environment that is necessary for grid reliability study.

An integrated power system simulation software program EPTOOL was developed. It is capable of analyzing power flow, small signal dynamics, and transient dynamics and prescribing dynamic controls. New power system components can be easily added and interfaced with EPTOOL. Impacts of protection devices on the system stability were modeled. These protective devices include over-current relays, different kinds of distance relays, under-voltage load shedding relays, and generator out-of-step relays. They are modeled to investigate the realistic events that may occur to power grids according to the adopted protection features. This software is applicable to both distribution systems and transmission systems.

Other features of EPTOOL include (1) analysis of oscillations caused by changes of operating conditions; (2) identifying critical subsystems that cause these oscillations; (3) prescribing dynamic controls that include (a) global robust control for single and/or multiple oscillations and (b) residue-based linear control to stabilize a specific mode with certain robustness. We conducted a pilot study and utilized the methodologies from probabilistic risk assessment for the first time. 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. EPTOOL has been used to provide support for the transient analysis for different fault scenarios.

This program was applied to study grid behaviors to find the root cause of the August 14th blackout. EPTOOL has also been extensively used to address various issues in transmission network as well as distribution systems in power grids. Stabilizing controls are synthesized to deal with voltage collapse and inter-area oscillation problems, which are the biggest concerns in grid studies, especially under deregulation.

SPECIFIC ACCOMPLISHMENTS:

Two papers were accepted to refereed conferences in FY 2004. A presentation of results to DOE was made in December 2003. A proposal was sent to DOE's new Office of Transmission Reliability on an assessment of the restoration process for the blackout of August 14, 2003. However, DOE's responsibility in this area was transferred to the industry organization, NERC.

LDRD FUNDING:

FY 2002	$ 83,965
FY 2003	$ 99,081
FY 2004	$103,512

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

Richard A. Ferrieri *02-045*
M. Thorpe

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, and N to certain environmental conditions.

APPROACH:

We are developing a radiotracer plant biology program that makes use of a suite of short-lived radiolabeled substances, administered to intact plants while maintained under tight environmental controls. In our laboratory we can administer $^{11}CO_2$ to leaves, as well as $^{13}NO_3^-$ and $^{13}NH_4^+$ to roots, all within a brief period of time. The diversity of sources is possible because of the Positron Emission Topography (PET) Facility's Ebco TR-19 and JSW 41 inch cyclotrons that can operate in unison for isotope production. Our developing work in plant biology represents a natural outgrowth for new applications of radiotracers and imaging in life science. The short-lived positron-emitting isotopes of carbon and nitrogen allow non-destructive and repeated measurement of the spatial distribution and transport dynamics of these tracers. Their short half-life (20.4 min for ^{11}C; 9.9 min for ^{13}N) prevents build-up of tracer in a plant so that labeling can be repeated indefinitely. The annihilation gamma radiation from tracer decay (511keV) penetrates plant tissue and soil, allowing detection of *in vivo* tracer.

Our facility's ^{11}C platform 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 CO_2 respiration as well as volatile organic hydrocarbon emissions, and mobile sugar fluxes within the plant. Mathematical analysis of these temporal tracer profiles allows continuous measurement of tracer transport dynamics, so that changes in tracer dynamics can be followed after diagnostic treatment of an intact plant. In the case of nitrogen, ^{13}N is the only radioactive isotope; for carbon, the other radioisotope ^{14}C is

inappropriate for non-invasive use as it has a low energy of decay, and also a long half-life (5000 yr), which makes repeated labeling impracticable. Furthermore, positron autoradiography allows us to repeatedly image and quantify nutrient allocation patterns across scales of the entire plant.

TECHNICAL PROGRESS AND RESULTS:

New Methodologies: Recently, we have developed two new methodological approaches adding new capabilities to coordinate plant biochemistry with physiology. Firstly, we have demonstrated that high specific activity $^{13}NH_3$ gas can be administered to intact leaves of plants, resulting in rapid assimilation of tracer into amino acids without altering leaf physiology. Just as carbon enters the plant metabolism *via* CO_2, all nitrogen enters (and re-cycles) via NH_3, with prior reduction from NO_3^-. Therefore, this tracer affords the unique opportunity to explore changes in leaf N metabolism as a function of environmental conditions. This aspect was demonstrated in a study using hybrid poplar, where leaf N metabolism was shown to be dependent on light intensity (Fig. 1).

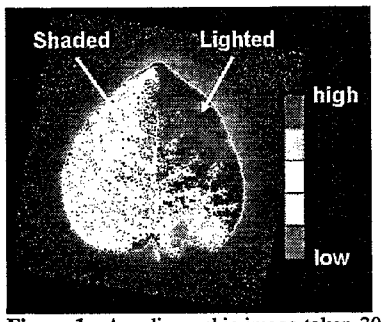


Figure 1. A radiographic image taken 30 min after leaf administration of $^{13}NH_3$. The shaded left-side of the leaf exhibited less tracer assimilation into amino acids.

Much of a plant's ability to survive depends on the exchange of water and nutrients between the rhizosphere and plant roots. Recently we demonstrated that it is possible to image and quantify root exudation of carbon derived from leaf [^{11}C]photosynthate. Maize plants, grown in rhizoboxes so that roots remain along the surface of the soil, could be subjected to radiographic imaging (Fig. 2) providing a measure not only of the axial root distribution of tracer, but through blot imaging, a measure of what tracer was released to the rhizospere.

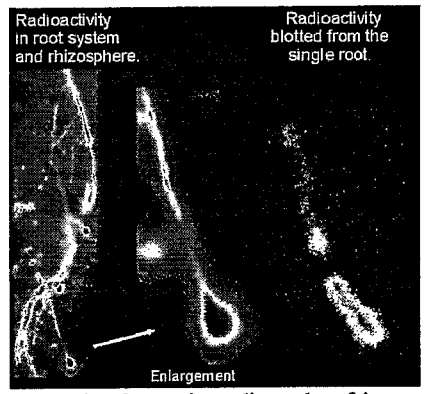


Figure 2. Composite radiographs of intact maize roots. The blot image showed that 1.5% of the axial root activity was released mostly at the root tip.

Investigations Linking Changes in Plant Biochemistry with Defense Response:
We've recently completed studies linking the effects of chemical defense inducement with changes in foliar biochemistry of recently fixed carbon, using the phytohormone jasmonic acid (JA). Last year, we reported that JA elicited both local and systemic responses resulting in alteration of leaf [^{11}C]photosynthate transport in *Populus tremuloides* and *Populus nigra* clones, with greater partitioning to roots after treatment. Further analyses revealed this action was due to a reduction of leaf starch pools with possible up-regulation of sucrose transporters. Furthermore, similar results were elicited when plants were subjected to attack by gypsy moth caterpillars.

This year, we extended this work to include a rigorous assessment of JA effects on leaf isoprene emission. Isoprene derives from a complex pathway involving leaf biochemistry of both recently fixed carbon and older carbon pools giving rise to terpenoids as well as other essential compounds including chlorophyll. We provided for the first time, evidence that JA caused both local and systemic elevations of isoprene emission (Fig. 3a,b).

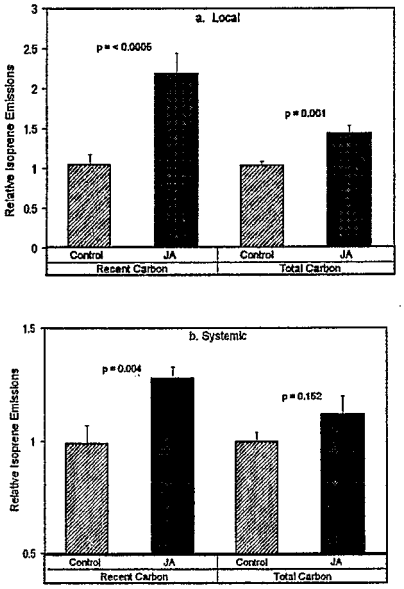


Figure 3. Local and systemic isoprene emissions relative to baseline response (prior to treatment) as a function of control and JA treatments.

More importantly, our results showed that the more recent carbon's contributions to isoprene emission, reflected by [^{11}C]isoprene, were more affected by the phytohormone action than the contributions from older carbon. This action may be implicated with an active defense response. Indeed, isoprene biosynthesis has been linked with an anti-oxidant defense mechanism associated with jasmonate biosynthesis.

We've also begun exploring the effects of JA defense inducement on plant nitrogen utilization by imaging root assimilation and whole-plant allocation of $^{13}NO_3^-$ (Fig. 4).

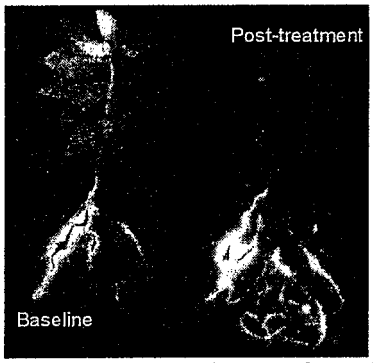


Figure 4. Radiograph images before and after JA treatment of entire foliage of *P. tremuloides* using $^{13}NO_3^-$ administered to an isolated lateral root.

Preliminary results suggest that plant utilization of nitrogen after JA treatment is reduced.

SPECIFIC ACCOMPLISHMENTS:

- **4 Peer reviewed publications in press or in review:**
  R.A. Ferrieri, D.W. Gray, B.A. Babst, M.J. Schueller, D.J. Schlyer, M.R. Thorpe, C.M. Orians, M. Lerdau "Use of Carbon-11 in Populus Shows that Exogenous Jasmonic Acid Increases Biosynthesis of Isoprene from Recently Fixed Carbon" *Plant, Cell & Environment* (in press; March 2005).

  J. Pritchard, A.D. Tomos, J.F. Farrar, P.E.H. Minchin, N. Gould, M.J. Paul, E.A. MacRae, R.A. Ferrieri, D.W. Gray, M.R. Thorpe "Turgor, Solute Import and Growth in Maize Roots Treated with Galactose" *Functional Plant Biology* 31: 1095-1103 (2004).

  B.A. Babst, R.A. Ferrieri, D.W. Gray, M.R. Thorpe, M. Lerdau, D. Schlyer, M. Schueller, C.M. Orians "Jasmonic Acid Induces Rapid Changes in Carbon

Transport and Partitioning in Populus" *New Phytologist* (in review).

M.M. Herth, M.R. Thorpe, R.A. Ferrieri "Synthesis of the Phytohormone [^{11}C]Methyl Jasmonate *via* Methylation on a C_{18} Sep Pak™ Cartridge" *J. Label Cmpds. & Radiopharm.* (in review)

- **6 Papers/Posters presented.**

Babst, B.A.; Ferrieri, R.A.; Thorpe, M. R.; Orians, C.M.; (2004). *Jasmonic Acid Increases Carbon Partitioning to Roots in Populus: Can Herbivory Induce Enhanced Tolerance?* 12th New Phytologist Symposium: Functional genomics of environmental adaptation in *Populus*, Portland, Oregon.

Gloser, V.; Ferrieri, R.A.; Orians, C.M.; (2004). Patchy Nitrate Availability Alone Contributes to Heterogeneous Responses in Plant Physiology and Chemistry Impacting Growth. National Meeting of Ecological Society of America. Portland, Oregon.

Babst, B.A.; Ferrieri, R.A.; Schlyer, D.J.; Schueller, M.; Orians, C.M. (2004). Jasmonic Acid Increases Carbon Partitioning to Roots in Populus: Can Herbivory Induce Enhanced Tolerance? National Meeting of Ecological Society of America. Portland, Oregon

Babst, B.A.; Ferrieri, R.A.; Gray, D.W.; Orians, C.M.; Schlyer, D.J.; Schueller, M.; Lerdau, M. (2004). Rapid Changes in Carbon Transport and Partitioning in Populus in Response to Jasmonic Acid. Gordon Research Conference, Plant Herbivore Interactions. Ventura, California

Lerdau, M.; Ferrieri, R.A.; Gray, D.W. Applications of Radiotracers in Plant Response Studies. Gordon Research Conference. Ventura, California

Ferrieri, R.A.; Ferrieri, A.P.; Thorpe, M.R. Up-regulating Plant Defenses in *Populus* Increases Phytoremediation of Carbon Tetrachloride. Abstract accepted to 8th International Symposium on In-Situ and On-Site Bioremediation, June 2005.

- **Multiple grant proposals submitted.**
  - USDA CRESS: "Characterizing the physiological mechanisms in soybean by which drought suppresses the symbiotic fixation of nitrogen." (not awarded)
  - NSF project proposal: "Whole-plant molecular integration of phloem translocation." (in review)
  - NSF project proposal: "Rapid whole-plant resource re-allocation in response to defense." (not awarded-resubmission 2005).
  - NSF FIBR pre-proposal accepted but full proposal not awarded — New pre-proposal accepted for 2005 competition - "Rhizosphere hyro-dynamics: Controls over carbon and nutrient cycling belowground."
  - DOE white paper. "Understanding the Physiological and Biochemical Basis for Controlling Carbon in Poplar Trees in Response to Nitrogen Metabolism."

LDRD FUNDING:

FY 2002	$ 99,220
FY 2003	$100,000
FY 2004	$149,232

Theory of Electronic Transport in Nanostructures and Low-Dimensional Systems

Alexei M. Tsvelik *02-070*
B. Narozhny
M. J. Bhaseen
R. M. Konik

PURPOSE:

The technical objective of the program is to provide an understanding of strongly correlated systems, in particular transport phenomena in low-D systems and quantum dots. We obtained non-perturbative results for conductivity of quantum dots in the presence of external scalar potentials leading to Fano resonances. Such resonances are experimentally observable and are an important tool for characterization of the interactions. This is related to the BNL effort in nanotechnology. The problem of confinement of fractional quantum number excitations in low-D systems has been studied. We established conditions for the existence of fractional quantum number excitations in dimensions greater than 1. We also developed a method for calculating correlation functions in the limit of weak confinement. This is related to the BNL effort in strongly correlated systems.

APPROACH:

Low-D systems may possess unconventional (topological) excitations with quantum numbers being a fraction of electron ones. Conditions for existence of such excitations and their experimental observability constitute a major problem of condensed matter physics. Measurements of transport properties is often the only probe available in dealing with nanosystems. We use such non-perturbative methods as Bethe ansatz, formfactor calculations etc. to calculate correlation functions of strongly correlated low-D systems, and in particular to describe their transport properties.

TECHNICAL PROGRESS AND RESULTS:

We calculated analytically correlation functions of several models with fractional quantum numbers in $D > 1$. These models are spatially anisotropic representing an ensemble of weakly coupled chains. The results imply that spinons may propagate incoherently in the direction perpendicular to the chains. This was done by Bhaseen and Tsvelik. The problem of Fano resonances in the Anderson model of quantum dots was solved by R. Konik.

A continuation of this work is anticipated, but the funding will come from the core program.

SPECIFIC ACCOMPLISHMENTS:

Publications:

Bhaseen, M.J.; Essler, F.H.L.; and Grage, A. "Itineracy effects on spin correlations in 1D Mott insulators." Phys. Rev. Lett. (submitted). BNL-72035-2004-JA

Bhaseen, M.J. and Tsvelik, A.M. "Aspects of confinement in low-dimensions." From Fields to Strings: Circumnavigating Theoretical Physics," Misha Shifman, Arkady Vainshtein, and John Wheater, Editors (World Scientific). BNL-73128-2004-BC

Konik R.M., "Kondo-Fano resonances in quantum dots: results from the Bethe ansatz," accepted in the letter section of the Journal of Statistical Physics.

Konik R.M., "Fano resonances in quantum dots: A non-perturbative role for potential-like scattering," Phys. Rev. B. (submitted).

Bhaseen, Miraculous J. and A. M. Tsvelik, "SU(N) evolution of a frustrated spin ladder." Phys. Rev. B68, 094405 (2003). BNL-71375-2003-JA

Narozhny, B.N.; Zala, Gábor, and Aleiner, I.L. "Interaction corrections at intermediate temperatures: dephasing time." Phys. Rev. B65, 180202 (2002). BNL 69243

Conferences:

Narozhny, B.N.; Zala, Gábor, and Aleiner, I.L. "Interaction corrections at intermediate temperatures: dephasing time," workshop in Strongly Correlated Systems, July 2002, ICTP

Tsvelik, A.M. and Bhaseen, M.J., "Propagating spinons beyond 1D," invited talk, APS March meeting, Austin, Texas 2003.

Tsvelik, A.M. and Bhaseen M.J., "Propagating spinons beyond 1D," invited talk, workshop on Quantum Criticality, Lorentz Center, Leiden, May 10-24, 2003.

Tsvelik, A.M. and Bhaseen, M.J., "Propagating spinons beyond 1D," invited talk, International Heraeus workshop on Quantum Field Theory in Condensed Matter and Particle Physics, MPIPKS Dresden, June 2-6, 2003.

Tsvelik, A.M. and Bhaseen, M.J., "How spin-1/2 imitates incommensurability," workshop on "Flux, Charge, Topology and Statistics," invited talk, University of Amsterdam, June 30 - July 5, 2003

Tsvelik, A.M. and Bhaseen, M.J., "Spinons beyond one dimension," invited talk, ICM-2003, Rome, July 26 - Aug. 1, 2003.

Tsvelik, A.M. and Bhaseen, M.J., "Spinons beyond one dimension," invited talk, The conference in tribute of Ian Kogan: Circumferencing Physics: from Fields to Strings, Oxford, Jan 8 - 10, 2004.

R.M. Konik, "Fano resonances in quantum dots," APS March meeting, Austin, Texas 2003.

Reports:

F.H.L. Essler and R.M. Konik, "Exact correlation functions in Condensed Matter Physics". "From Fields to Strings: Circumnavigating Theoretical Physics," Misha Shifman, Arkady Vainshtein, and John Wheater, Editors (World Scientific).

LDRD FUNDING:

FY 2002	$134,268
FY 2003	$115,000
FY 2004	$148,483

Pressure in Nanopores

Thomas Vogt *02-071*
Y. Lee

PURPOSE:

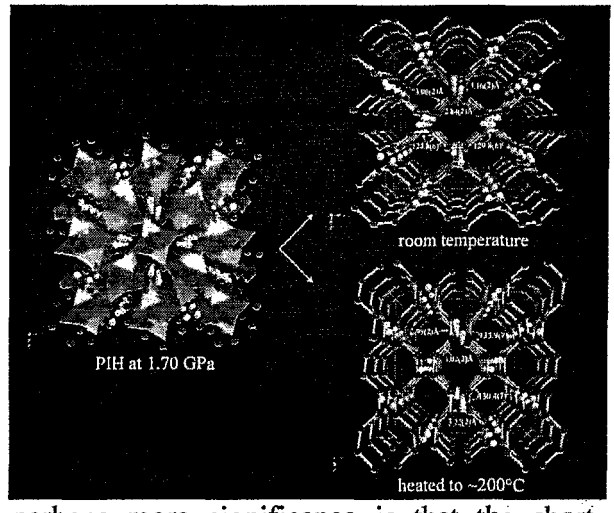
The purpose of this project is to study the structural changes in nano-confinement, which result from pressure-induced chemical reactions or intercalations within nanopores, channels, and layers. Various interactions between the species, inherent in a given nanosystem and introduced under pressure, leads to unusual property changes and formation of ordered nanostructures, which may open new types of applications of these materials.

APPROACH:

Use micro-focused monochromatic synchrotron X-ray powder diffraction and diamond-anvil high-pressure cells available at beamline X7A of NSLS. This permits structural studies to be carried out using either the Rietveld technique or an *ab initio* structure solution. We also use a hydrothermal DAC or He refrigerator to extend our thermodynamic space into simultaneous P-T regions. In addition, pressure effects on nanolayer systems and nanoparticles are currently investigated in collaborations that include J.A. Hriljac (U Birmingham, UK), V. Petkov (CMU), S.-W. Chan (Columbia Univ.), H. ZurLoye (USC), A. Ulman (Polytech Univ.).

TECHNICAL PROGRESS AND RESULTS:

The experimental confirmation of reversible and irreversible pressure-induced hydration (PIH) in zeolites with the natrolite topology demonstrates how hydrostatic pressure can be used to control water content and assemble unique water structures within the confinement of nanometer sized channels and pores created by an aluminosilicate framework. The 'superhydrated' phase of natrolite at 1.7 GPa shows that a unique nanowater structure, a 4_1 water spiral along the c-axis with alternating O-O distances of 2.84(2) Å and 3.16(2) Å enclosing sodium cations, has formed within the pores. Of



perhaps more significance is that the short cross-channel oxygen-oxygen distance of 3.06(2) Å indicates the presence of 1-dimensional water wires running *perpendicular* to the *b*-axis. By increasing the temperature under pressure we are able to reversibly manipulate and alter the orientation of these ordered water wires due to the anisotropic thermal expansion of the host scaffolding. At about 200°C at 1.7 GPa the water wires are now aligned *parallel* to the *b*-axis with the oxygen-oxygen distances (2.99(2)Å and 3.02(2) Å) along the wire being the same within the estimated standard deviations. We conjecture that the reversible change in the direction of the shortest oxygen-oxygen distances will lead to a concomitant switch in the direction of the protonic current. This could provide an intriguing gating mechanism and proof of principle for a proposed switchable nanoscale semi-conductor.

SPECIFIC ACCOMPLISHMENTS:

Invited talks

1. Pressure-induced stabilization of ordered paranatrolite: a possible solution to the

paranatrolite controversy. In *the Advanced Characterization of the Structures and Behaviors of Minerals Session*, the 2004 Geological Society of America Annual Meeting, Denver, CO. Nov. 7, 2004.

2. Pressure-induced hydration of zeolites in the natrolite family. Geophysical Laboratory, Washington, D.C., Sep. 2, 2004.

Publications

1. Drymiotis, F.R.; Lee, Y.; Lawes, G.; Correa, V.; Kimura, T.; Migliori, A.; Lashley, J.C.; Shapiro, S.M.; Fisher, R.A. (submitted) *Tunable Thermal Expansion Behavior in the Intermetallic YbGaGe.* **Phys. Rev. B.**

2. Mudryk, Y.; Lee, Y.; Vogt, T.; Gschneidner, Jr. K.A.; and Pecharsky, V.K. (accepted) Polymorphysm of *Gd5Si2Ge2 – the equivalence of temperature, magnetic field, and chemical and hydrostatic pressures.* **Phys. Rev. Lett.**

3. Park, S.; Lee, Y.; and Vogt, T. (accepted) Structural Distortion and Disappearance of Layer Ordering in $Li_xCoO_2 2H_2O$. **Phys. Rev. B.**

4. Lee, Y.; Hriljac, J.A.; and Vogt, T. (in press) Variable-temperature structural studies of tetranatrolite from Mt. St. Hilaire; Synchrotron X-ray powder diffraction and Rietveld analysis. **Am. Mineral.**

5. Lee, Y.; Hriljac, J.H.; Parise, J.B.; and Vogt, T. (in press) Pressure-induced stabilization of ordered paranatrolite: a possible solution to the paranatrolite controversy. **Am. Mineral.**

6. Yang, X.; Camblor, M.A.; Lee, Y.; Liu, H.; and Olson, D.H. (2004) *The synthesis and structure of as-made and calcined pure silica zeolite ITQ-12.* **J. Am. Chem. Soc.,** 126, 10403-10409.

7. Colligan, M.; Forster, P.M.; Cheetham, A.K.; Lee, Y.; Vogt, T.; and Hriljac, J.A. (2004) *Synchrotron X-ray powder diffraction and computational investigation of purely silicious zeolite Y under pressure.* **J. Am. Chem. Soc.** 126, 12015-12022.

8. Lee, Y.; Hriljac, J.A.; and Vogt, T. (2004) *Pressure-induced migration of zeolitic water in laumontite.* **Phys. Chem. Mineral,** 31: 421-428.

9. Lee, Y.; Martin, C.D.; Parise, J.B.; Hriljac, J.A.; and Vogt, T. (2004) *Formation and manipulation of confined water wires.* **Nano Lett.** 4, 619-621.

10. Lee, Y.; Hriljac, J.A.; Studer, A.; and Vogt, T. (2004) *Anisotropic compression of edingtonite and thomsonite to 6 GPa at room temperature.* **Phys. Chem. Mineral.** 31, 22-27.

11. Jeong, I.-K.; Darling, T.W.; Graf, M.J.; Proffen, T.; Heffner, R.H.; Lee, Y.; Vogt, T.; and Jorgensen, J.D. (2004) *The role of the lattice in the Ce gamma-alpha phase transition: a high pressure neutron and x-ray diffraction study.* **Phys. Rev. Lett.** 92, 105702.

12. Kennedy, B.J.; Li, L.; Lee, Y.; and Vogt, T. (2004) *Pressure induced valence and structural phase transition in Ba2PrRu1-xIrxO6.* **J. Phys.: Condens. Matter.** 16, 3295-3301.

13. Park, S.; Lee, Y.; and Vogt, T. (2003) *Novel synthesis and high pressure behavior of NaxCoO2yH2O and related phases.* **Phys. Rev. B.** 68, 180505(R).

LDRD FUNDING:

FY 2002	$ 79,000
FY 2003	$ 82,600
FY 2004	$ 57,423

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

APPROACH:

The SELEX approach 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.

Due to the insolubility of the MerR family regulators, we abandoned the SELEX approach and exploited an alternative to analyse interactions between MerR-family regulators, their specific promoters and their metal specificity, this in collaboration with C. He (University of Chicago).

TECHNICAL PROGRESS AND RESULTS:

Phylogenetic analysis of heavy metal resistance regulators. After a basic local alignment search tool (BLAST) search of the nearly completed sequenced genome of *Ralstonia metallidurans* CH34, 10 PbrR/MerR like regulators were identified. The *mer*R-like and *pbr*R-like regulators were cloned with and without His-tag fusions in pET28 and pET30 and checked for their over-expression.

It turns out that most MerR-family regulators are not soluble in low salt, aqueous solution, unless they are bound as dimmers to their specific promoter region DNA. This makes them unsuitable for SELEX enrichment for DNA fragments. We therefore used a different strategy to study the interaction of these proteins with their DNA fragments. For this work we concentrated on PbrR691 of the chromosomal *pbr*RAC operon, a protein which we were able to express and purify.

A 25-mer duplex DNA containing the PbrR691 binding sequence was synthesized. A pyrrolo-C base, which has fluorescent properties that are quenched when this nucleotide is bound to a G base in its complementary DNA strand, was incorporated into the central part of this sequence (DNA-1 in Figure 1). This duplex DNA exhibits weak fluorescence as expected. Addition of one equivalent of Pb^{2+} per PbrR691 dimer triggered a significant fluorescence enhancement within seconds. (Figure 2A) The sensor is selective as addition of 50-fold excess of Zn^{2+}, Co^{2+}, Hg^{2+}, Cu^{2+}, and Cd^{2+} caused less than 1/20 of the fluorescence increase at 445 nm compared to that for Pb^{2+}. The fluorescence response of the PbrR691-based sensor to Pb^{2+} appears to be over 1000-fold higher than that to other metal ions in this assay (Figure 2B). Thus, PbrR691 is highly selective towards lead(II). We want to point out that other heavy metal ions may bind to PbrR691; however, the binding does not seem to trigger the conformation change of the protein that is required to distort the promoter DNA. Thus, besides providing a

selective lead(II) sensor, the system described here offers a simple method to reveal the "real" selectivity of PbrR691.

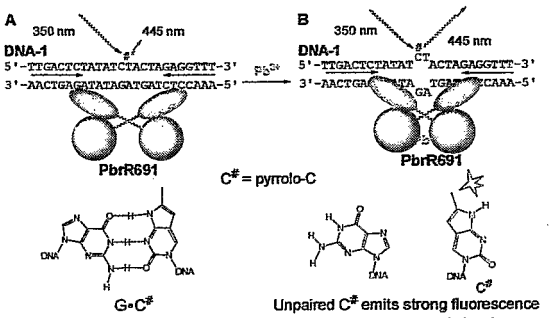


Figure 1. (A) Pyrrolo-C can form a stable base pair with G. The fluorescence intensity of pyrrolo-C is quenched in the duplex DNA. The promoter sequence that PbrR binds is used to construct DNA-1; the dyad symmetrical sequence is marked with arrows. (B) Binding of Pb^{2+} to PbrR691 induces base-unpairing of pyrrolo-C, which emits strong fluorescence at ~445 nm upon excitation.

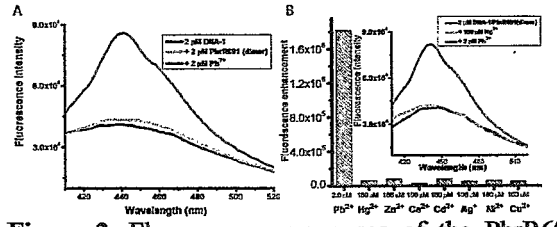


Figure 2. Fluorescence responses of the PbrR691-based fluorescent biosensor toward different metal ions. (A) Fluorescence spectra of the biosensor in the absence and presence of one equivalent of Pb^{2+} ion. (B) The fluorescence enhancement integrated from 420 to 500 nm in the presence of 2 μM of Pb^{2+} and 100 μM of other metal ions. The insert presents the fluorescence spectra of the sensor in the presence of 2 μM of Pb^{2+} and 100 μM of Hg^{2+}.

This strategy is presently being employed to analyze the specificities of promoter recognition and metal binding of the different MerR-family proteins identified in *Ralstonia metallidurans* CH34.

SPECIFIC ACCOMPLISHMENTS:

Development, in collaboration with C. He, of a very sensitive test system to analyze the specificities of promoter recognition and metal binding of the different MerR-family proteins identified in *Ralstonia metallidurans* CH34 is presently being recorded in a record of invention.

Monchy, S.; Auquier, V.; Van Aelst, S.; Vallaeys, T.; Benotmane, M.A.; van der Lelie, D.; Taghavi, S.; Wattiez, R.; and Mergeay, M. Organization of heavy metal resistance genes in the four replicons of *Ralstonia metallidurans*. Plasmid (in press).

Chen, P.; Greenberg, B.; Taghavi, S.; Romano, C.; van der Lelie, D.; and He, C. A novel lead (II) regulatory protein in *Ralstonia metallidurans*: development of a ratiometric fluorescent lead (II) sensor. Angewandte Chemie, International Edition (submitted).

LDRD FUNDING:

FY 2002	$163,972
FY 2003	$170,900
FY 2004	$161,662

Lead Resistance in *Ralstonia metallidurans* CH34

Safiyh Taghavi *02-084b*

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, located on plasmid pMOL30 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 and characterize different *pbr* mutants.

To study the functioning of the *pbr* proteins, we cloned them into a pET protein expresion system.

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 that are present on the CH34 chromosome.

TECHNICAL PROGRESS AND RESULTS:

Isolation of *pbr* mutants. We used the EZ::Tn(Km2) *in vitro* transposition system to construct a library of *pbr*::Tn(Km2) mutants. Approximately 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 *pbr*R 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, *pbr*B was the only gene indispensable for lead resistance. Three other *pbr* genes, the regulator *pbr*R and the structural genes *pbr*A and *pbr*C, have chromosomal counterparts in the *pbr*RAC operon, which can presumably complement their activities. Quantitative PCR on the lead induced transcriptome of CH34 showed that in the early hours after the addition of Pb^{2+}, the transcription of the chromosomally located resistance *pbr*RAC operon went up. In the presence of higher Pb^{2+} concentrations the activities of the pMOL30 located *pbr*TRABCD operon was induced as the ultimate, indispensable line of defense. This was confirmed with 2D gel electrophoresis that showed the presence of the different Pbr proteins after Pb^{2+} induction.

Further analysis of the PbrB protein showed that it is an acid phosphatase. Our working hypothesis is that PbrB liberates a phosphate from an organic compound, most likely a phospholipid, and that the phosphate is used to precipitate the lead that is exported by the PbrA lead efflux ATPase. Unfortunately, preliminary X-ray absorption fine structure (EXAFS) spectroscopy studies were unable to confirm the formation of lead phosphate when PbrB was expressed. This analysis will be completed.

Phylogenetic analysis of PbrR-like regulators. After a basic local alignment search tool (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 in four major groups.

Structure of MerR / PbrR proteins. It has been impossible so far to obtain crystals of MerR and PbrR proteins and to use them for determining the crystal structures of these proteins. A total of 10 *mer*R-like and *pbr*R-like regulators were cloned as His-tag fusions in pET28 and pET30 and checked for over-expression. One protein, referred to as MerR663 (mercury resistance regulator) was purified and checked for its stability. Subsequently, in collaboration with C. He at the University of Chicago, the MerR663 protein was crystallized. Presently, the MerR663 structure is being analyzed by crystal diffraction at Argonne National Laboratory. We chose this protein, as we were able to produce it in high, soluble quantities. On the other hand, we had problems to purify some as the MerR like proteins, such as PbrR form the *pbr*TRABCD operon, as they tended to form insoluble complexes upon over-expression in *E. coli.* The collaboration with C. He resulted for the first time in obtaining crystals of a MerR protein.

Design of lux-based bacterial biosensors. 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 and the Limburgs Universitair Centrum.

SPECIFIC ACCOMPLISHMENTS:

Publications

Vangronsveld, J. and van der Lelie, D. The use of alternative techniques for remediation of polluted sites and groundwater in Flanders: plant-based strategies. J. Soil Sediments 3, 250-251 (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 161, 549-555 (2004).

Renella, G.; Mench, M.; van der Lelie, D.; Pietramellara, G.; Ascher, J.; Ceccherini, T.; Landi, L.; and Nannipieri, P. Hydrolase activity, microbial biomass and community structure in long-term Cd-contaminated soils. Soil Biol. Biochem. 36, 443-451 (2004).

Vassilev, A.; Schwitzguebel, J.-P.; van der Lelie, D.; and Vangronsveld, J. The use of plants for remediation of metal contaminated soils. The Scientific World J. 4, 9-34 (2004).

Everhart, J.L.; van der Lelie, D.; Chaney, R.L.; and Sparks, D.L. Assessing nickel bioavailability in smelter-contaminated soils. Plant Soil (submitted).

Nachtegaal, M.; Marcus, M.A.; Sonke, J.E.; Vangronsveld, J.; Livi, K.; van der Lelie, D.; and Sparks, D.L. Effects of *in situ* remediation on the speciation and bioavailability of zinc in a smelter contaminated soil. Geochim. et Cosmochim. Acta (submitted).

Follow-On Funding:

The Impact of Surface Precipitation on Sequestration and Bioavailability of Metals in Soil. Center for the Study of Metals in the Environment at the University of Delaware. D. Sparks and D. van der Lelie, P.I.s, FY 2005, $49,600.

LDRD FUNDING:

FY 2002	$161,408
FY 2003	$170,100
FY 2004	$169,708

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/cm^2 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 proposed ultrafast x-ray source was completed in FY04. Preliminary testing of the source was then carried out. X-rays were generated by focusing the regenerative amplified Ti:Sapphire laser beam onto the moving wire cooper (Cu) target. The wavelength of the characteristic emission line of Cu, ~1.5 Angstrom is well matched to the planned ultrafast x-ray diffraction experiments. The integrated intensity of Cu Kα radiation was measured by using a combination of aluminum foil, acting as a high pass filter, and a thin Si photodiode detector, which also acts as a low pass filter due to its low quantum efficiency for high energy x-rays. With 35 mJ, 120 fs, and 800 nm excitation pulses from the regenerative amplified Ti:Sapphire laser, an x-ray flux of ~10^8 Kα photons/(s 4pi sr) was measured. This number agrees well with the projected value and is sufficient to begin an experimental program. However, an upgrade of the laser system to increase the repetition rate will be desirable.

To completely characterize the ultrafast x-ray source, it is essential to develop experimental methods to measure the pulse length directly. In this direction, we have investigated the possibility of using x-ray streak camera as well as using cross correlation of the pump-laser and the x-ray source. Streak camera is going to be useful if the x-ray pulse length is on the order of 1 ps. Cross correlation technique would allow us to measure significant shorter pulses. We will pursue both options since the expected pulse length is ~0.5 ps.

Finally, we have also begun the design of x-ray focusing optics to couple the ultrafast x-rays to the sample for different experimental configurations. For ultrafast diffraction experiments, a horizontal cylindrically bent Si crystal is designed to be used both as the monochromator as well as the focusing element to collect a large solid angle of the radiation and to provide a line focus on the sample. For x-ray absorption experiments, several possible configurations have been considered. In the first case, a channel-cut Si monochromator followed by a glass capillary lens will be used. This configuration is less efficient, but important for the study of a dilute sample where a measureable fluorescent yield is necessary. In the second case, a dispersive setup using a bent Si crystal will be used. This configuration has the advantage of parallel detection of the whole absorption spectrum but is limited to the study of concentrated samples. Finally, a new scheme has been developed to allow simultaneous energy dispersive and fluorescent detection. The development of this combination will be important for a large number of future ultrafast excited spectroscopy studies because the excited state population is usually kept as low as possible to avoid sample damage (needs fluorescent detection), and the uncertainty in the spectral content from shot-to-short (need energy dispersive). Moreover, this detection scheme will also benefit existing x-ray absorption programs at the NSLS.

The proposed ultrafast x-ray source has been completed. This new source could be used to enable new research programs in the Laboratory.

SPECIFIC ACCOMPLISHMENTS:

These results were presented at the "Workshop on Ultrafast X-ray Sciences" and the BNL Center for Functional Nanomaterials Users' meeting.

LDRD FUNDING:

FY 2002	$100,018
FY 2003	$105,000
FY 2004	$104,578

X-ray Photon Correlation Spectroscopy Studies of Nanostructured Block Copolymers

Steve Dierker *02-088*

PURPOSE:

The objective of this 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 phase separated.

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 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 have developed a 2D gas detector which has high quantum efficiency, high speed readout, and high position resolution. This was done in collaboration with Graham Smith in the Instrumentation Division. The detector has been developed and refined through several prototypes. We also developed 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 NSLS for another gas detector developed there for high throughput powder diffraction.

The new detector is ready to be used in experiments in the coming year. The 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:

Two publications based on this work are in preparation for submission.

LDRD FUNDING:

FY 2002	$ 90,212
FY 2003	$105,000
FY 2004	$104,775

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 risky, cutting edge research and development (R&D), but the payoff could be high in enabling new radiation sources such as x-ray free electron lasers (FELs), Photoinjected Energy Recovery Linacs, electron cooling for RHIC, and high-power FELs for defense applications.

APPROACH:

The PI, in collaboration with Triveni Srinivasan-Rao and Andrew Burrill, undertook to carry out the development of superconducting laser photocathode radio frequency (RF) guns and the associated laser illumination system. To generate high brightness and high power electron beams, two essential criteria need to be met. The first is the generation of a high current beam which requires the development of a high quantum efficiency (QE) photocathode and associated laser. The second is an acceleration of the electron beam to high energy with existing RF sources that requires the development of superconducting injectors. This research program is being carried out through two separate research paths: the all niobium superconducting RF photoinjector and the high average current multi-alkali photocathode deposition program. The all niobium superconducting radio frequency (SCRF) photoinjector allows for CW operation while the multi-alkali photocathode with its high QE at visible wavelengths allows for generation of very high current electron beams due to the high QE of these cathodes.

TECHNICAL PROGRESS AND RESULTS:

In FY 2004 significant results were achieved with the SCRF photoinjector. The cryostat, containing the all Nb superconducting injector, was cooled down to 4K and 2K several times, and the frequency Q and maximum field sustained by the cavity were measured. Figure 1 illustrates the dependence of the Q on the temperature of the cavity.

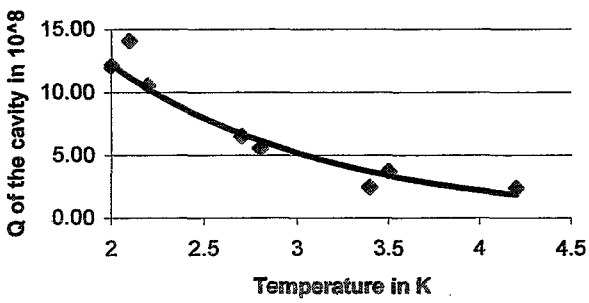


Figure 1. Q_0 of the all Nb SC injector as a function of cavity temperature

The superconducting cavity was irradiated by two lasers, one with a photon energy of 5 eV, pulse duration of 12 ns and repetition rate up to 200 Hz, and another with photon energy of 4.66 eV, a pulse duration of 7 ps and repetition rate of 81.25 MHz, 1/16th the frequency of the cavity. This laser was phase locked to the RF such that the laser arrives at the correct RF phase. The photo-emitted electrons were transported through the beam pipe, focused by the solenoid on the Faraday cup, and the current and QE were measured using both the lasers. The quantum

efficiency of the SC Nb was measured for the first time and was found to be $2x10^{-6}$ for 4.66 eV photons and $2x10^{-5}$ for 5 eV photons, both an order of magnitude lower than those measured at room temperature. A multialkali has been tested successfully and is in operation producing cesium potassium antimonide cathodes on molybdenum substrates. To date approximately 40 cathodes have been produced with uniform emitting surfaces and quantum efficiencies of 2-3 % at 548 nm (2.27 eV). The QE, uniformity of emission and lifetime are shown in Figures 2, 3 and 4.

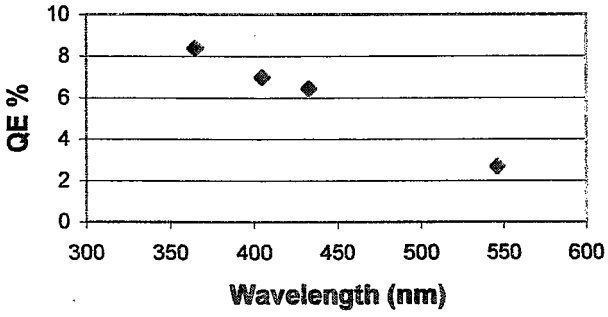


Figure 2: QE as a function of wavelength using Xe-Hg lamp and monochromator

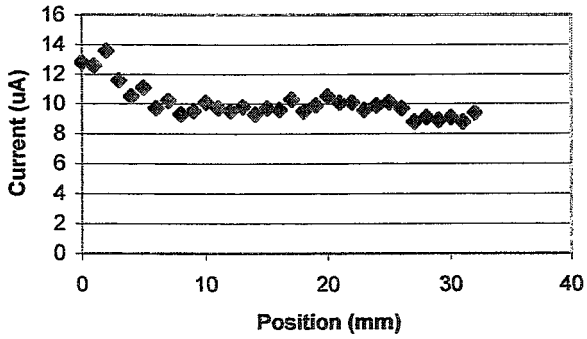


Figure 3. Uniformity of emission over the cathode diameter. The laser beam was focused to 100 micron to simulate the current densities needed for e cooler

These results illustrate that uniform, high photocurrent can be generated reliably to meet the requirements of the e cooler with commercially available laser systems.

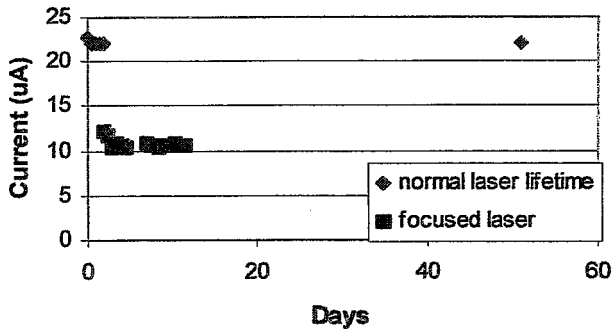


Figure 4. Life time of the cathode in the deposition chamber for unfocused, few mm and focused 100 micron diameter beam.

In the next phase, the means of combining these two research paths to develop a single system capable of delivering an electron beam with both high brightness and high power will be investigated. One of the important issues to be addressed is the performance of both the cavity and the cathode in the presence of one another. Contamination of the cavity with Cs and contamination of the cathode with cavity impurities will both be detrimental to the overall performance. Possible use of diamond to isolate the cavity from the cathode as well as to amplify the current from the cathode are presently under investigation.

There is a growing interest in the community of photoinjectors to produce a superconducting photoinjector capable of ampere-class current. Successful incorporation of a multialkali cathode with diamond amplifier/barrier may pave the way for such an injector.

SPECIFIC ACCOMPLISHMENTS:

Publications:

I. Ben-Zvi, A. Burrill, R. Calaga, P. Cameron, X. Chang, D. Gassner, H. Hahn, A. Hershcovitch, H.C. Hseuh, P. Johnson, D. Kayran, J. Kewisch, R. Lambiase, V.

Litvinenko, G. McIntyre, A.Nicoletti, J. Rank, T. Roser, J. Scaduto, K. Smith, T. Srinivasan-Rao, K.-C. Wu, A. Zaltsman, Y.Zhao, H. Bluem, A. Burger, M. Cole, A. Favale, D. Holmes, J. Rathke, T. Schultheiss, A. Todd, J. Delayen, W. Funk, L. Phillips, J. Preble, "AMPERE AVERAGE CURRENT PHOTOINJECTOR AND ENERGY RECOVERY LINAC," presented at 26th Intl FEL conf. Trieste, Italy, Aug. 29 – Sept. 3, 2004

V. N. Litvinenko, I. Ben-Zvi, D. S. Barton, D. Beavis, M. M. Blaskiewicz, M. Brennan, A. Burrill, R. Calaga, P. Cameron, X. Chang, R. Connolly, D. M. Gassner, H. Hahn, A. Hershcovitch, H.-C. Hseuh, P. Johnson, D. Kayran, J. Kewisch , R. Lambiase, W. Meng, G. Mahler, G. McIntyre, T. C. Nehring, A. Nicoletti, D. Pate, J. Rank, T. Roser, T. Russo, J. Scaduto, K. S. Smith, T. Srinivasan-Rao, N. W. Williams, K.-C. Wu, V. Yakimenko, K. Yip, B. A. Zaltsman, Y. Zhao, C. H. Bluem, A. Burger, M. Cole, A. Favale, D. Holmes, J. Rathke, T. Schultheiss, A. Todd, J. Delayen, W. Funk, P. Kneisel, L. Phillips, J. Preble, "High Current Energy Recovery Linac at BNL," presented at 26th Intl FEL conf. Trieste, Italy, Aug. 29 – Sept. 3, 2004

Ilan Ben-Zvi*, Joseph Brennan, Andrew Burrill, Rama Calaga, Xiangyun Chang, Gregory Citver, Harald Hahn, Michael Harrison, Ady Hershcovitch, Animesh Jain, Christoph Montag, Alexei Fedotov, Joerg Kewisch, William Mackay, Gary McIntyre, David Pate, Stephen Peggs, Jim Rank, Thomas Roser, Joseph Scaduto, Triveni Srinivasan-Rao, Dejan Trbojevic, Dong Wang, Alex Zaltsman, Yongxiang Zhao, "R&D towards cooling of the RHIC Collider," Nuclear Instruments and Methods in Physics Research A 532 (2004) 177–183.

LDRD FUNDING:

FY 2003	$150,000
FY 2004	$192,464
FY 2005 (budgeted)	$190,000

Feasibility Study of the Optical Stochastic Cooling with a CO_2 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 to test SC are planned for the near future. OSC has the potential to affect the whole beam contrary to SC, which only deals with a small portion of the beam. OSC is complimentary to electron cooling (EC), which is another RHIC cooling project. EC is more effective for the particles with small amplitudes, while OSC works faster at large amplitudes. Thus addition of the OSC to the EC would dramatically reduce the 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 high power pulsed CO2 laser, we intend to characterize the amplification of a CW CO2 laser at 9 microns. Demonstration of successful amplification using this OPA will allow us to extrapolate the performance expected under the conditions required for optical stochastic cooling of RHIC. Experiments using the output of the JLAB FEL (Free electron Laser) as a pump source for OPA would allow testing an optical amplifier at full power load are complimentary to this activity and are planned as part of another LDRD.

TECHNICAL PROGRESS AND RESULTS:

The originally considered several dozen meter long gas laser based amplifier is replaced 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. We use an OPA based GaGeAs2 crystal as an optical amplifier for the OSC. A test stand was designed and assembled to verify performance of the OPA in the low repetition (low thermal load) mode of operation. A small amplification was observed. An understanding of the very challenging alignment procedure led to a significant modification of the test stand. Experimental verification of the phase preservation during OPA with relaxed alignment requirements, due to enlarged laser sizes, is in its final stages of development.

We started the design of the CO_2 based pump source. It consists of a mode locked CO_2 based oscillator at 10 MHz and a commercially available CW CO_2 welding lasers. Experimental tests of the mode locked CO_2 based oscillator, is the last item in the optical amplifier part of OSC project that needs verification.

SPECIFIC ACCOMPLISHMENTS:

Publications:

1. 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. Zolotorev, Phys.

Rev. ST Accel. Beams volume 7, issue 1, 012801 (2004).
2. M. Babzien, I. Ben-Zvi, I. Pavlishin, I. V. Pogorelsky, V. E. Yakimenko, A. A. Zholents, and M. S. Zolotorev, Optical Stochastic Cooling for RHIC, To be published in NIM.
3. M. Babzien, I. Ben-Zvi, I. Pavlishin, I. V. Pogorelsky, V. E. Yakimenko, A. A. Zholents, and M. S. Zolotorev, Optical Stochastic Cooling for RHIC, Workshop on Beam Cooling and Related Topics, Mt. Fuji, Japan, May 19-23, 2003.

LDRD FUNDING:

FY 2003	$110,000
FY 2004	$121,834

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 Nb_3Sn 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 Nb_3Sn. 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 Nb_3Sn superconductor, which becomes brittle after reaction. Our plan here was to make two concentric coils with 7 and 9 slots respectively. We used the small amount of ITER (International Thermo-nuclear Experimental Reactor) material already available at BNL for an early start on the construction of a coil, and then planned to 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 was cabled, reacted, and insulated. This procurement proved difficult because of the long lead times at the manufacturers. Because of a lack of orders, the manufacture of Nb_3Sn wire is not yet a well developed industrial process. 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 were 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.

New superconductor wire became available and the winding of the slots was to resume and the ability to reach the expected short sample performance was to be studied more extensively. All the slots of the inner form were to be filled with the superconductor and powered to study performance. If this were successful the outer coil form would have been machined, and it too would have been filled with the superconductor and

tested. Then the coils were to be assembled together and tested as a completed magnet.

Unfortunately, the new material proved in short sample tests to be unstable and not usable in a magnet. This spurred tests that revealed that the large filament size was the likely source of instability. Interaction continues with the manufacturer to improve this parameter and to deliver usable wire. Understanding this shortcoming is an important step towards using Nb3Sn in future magnets.

SPECIFIC ACCOMPLISHMENTS:

A report was written on the test results (MDN-635-36, Evaluation of SonicBond Prepreg in Slotted Windings, E. Willen, BNL, April, 2004).

LDRD FUNDING:

FY 2003	$147,800
FY 2004	$156,269

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

Brett Parker *03-014*

PURPOSE:

The BNL Magnet Division pioneered direct-wind technology with precise placement of superconducting cable under computer control. It was used in making interaction region (IR) magnets for the Hadron Electron Ring Accelerator (HERA-II) and Beijing Electron Positron Collider (BEPC-II) Luminosity Upgrades. For a future linear collider the IR magnet coils should be compact enough that with a moderate beam crossing angle the disrupted beam leaving the IR can pass outside the magnet while the inbound beam inside the magnet receives strong focusing. In this LDRD we looked to extended this technology to be able to make superconducting quadrupoles with a five times smaller aperture but ten times higher gradient than before.

APPROACH:

The main coil production challenges were to learn to reliably wind tight conductor bends and to develop coil structures that minimize dead space given over to cable insulation, fiberglass wrap and epoxy filler. We proceeded by making a series of winding tests on small diameter coil support tubes. Some examples are shown in Figure 1. Many winding issues were confronted and ultimately resolved by invention of a new coil topology, the Serpentine Planer Hybrid, not anticipated in the original proposal.

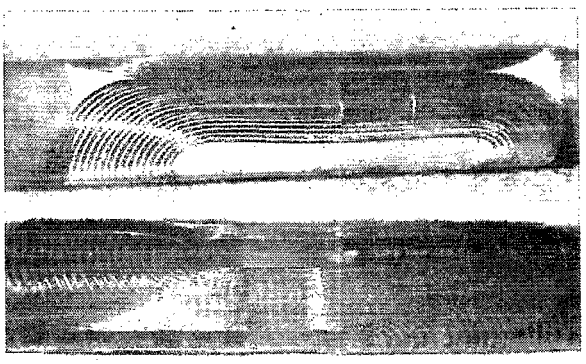


Figure 1. Early test windings. Upper is planar single layer dipole pattern. Lower is Serpentine dual-layer quadrupole pattern with nested straight section turns.

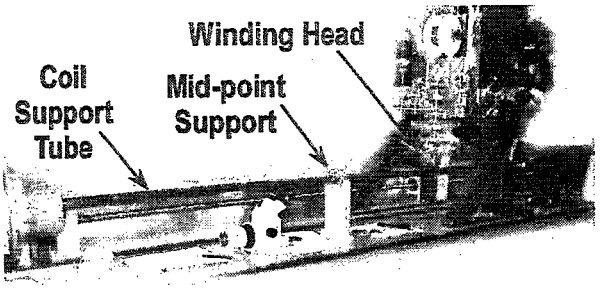


Figure 2. BNL direct-wind machine with NLC coil winding in progress. Mid-point support is visible.

TECHNICAL PROGRESS AND RESULTS:

After initial success winding coils with tight bends using standard winding patterns similar to the upper pattern in Figure 1, it became apparent that such patterns were not suitable for making multi-layer coil structures with good packing efficiency; and when we attempted coils more than 1 m long, flexing of the spaghetti-like support tube made conductor placement difficult. Flexing was dealt with by adding mid-point support as shown in Figure 2. Coil packing

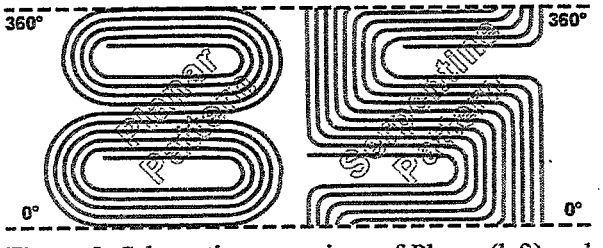


Figure 3. Schematic comparison of Planar (left) and Serpentine style winding. Planar can be lifted from support tube without cutting conductor; a Serpentine pattern winds continuously around the tube.

improvement came about during continuous evolution in winding technique.

Figure 3 shows a schematic comparison of planar (i.e. HERA-II style) and Serpentine coil patterns. A planar coil pattern can be laid down on a sheet without lifting and the conductor is ultimately trapped in the pole region. It takes extra radial space to get magnet leads out flat over the coil pack. Tight bends, that risk conductor damage, are needed to do this and the leads remain vulnerable to damage during later handling.

Serpentine patterns avoid trapping conductor by going around the tube 360° to come back to where winding started. Each turn can then lay next to turns already laid down. Since Serpentine winding goes from one side of the coil pack to the other, by winding an even number of Serpentine layers we guarantee that both leads end up on the same side of the coil pack. The leads are brought out without sharp bends or wasting radial space. We reverse the winding direction in alternate layers to avoid making solenoidal fields. End turns in neighboring layers cross as shown at the bottom of Figure 1.

The dual-layer Serpentine pattern in Figure 1 is also special in that the turns of the straight section of the upper layer lay in the "groove" between the turns of the lower layer. Naively this might seem to improve radial packing, but in the coil ends there are always places where conductors must cross each other and two full wire diameters of radial buildup are then required. Real packing improvement is accomplished here by winding two layers that share one fiberglass compression wrap. With the coil thickness growing faster in the ends than in the middle straight section, nested winding is not a useful improvement. A subsequent long coil, taken to SLAC for review by the International Technology Review Panel (ITRP), was successfully wound as two Serpentine style layers without nesting.

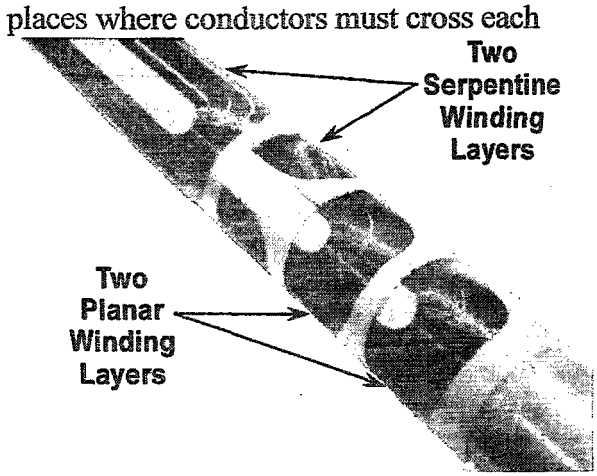


Figure 4. Four layer coil set demonstration winding.

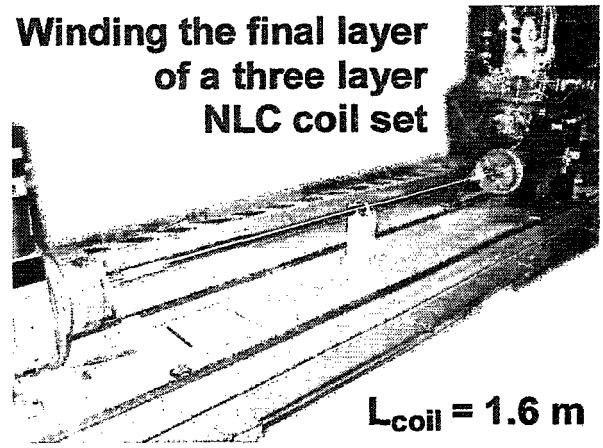


Figure 5. Winding the 1.6 m three layer NLC coil

When this coil was returned to BNL we decided to strip these layers because new substrate material became available that allowed us to improve the ground plane and turn-to-turn insulation, and we developed a scheme to wind coils in three- or four-layer groupings (here denoted a coil set) at one time. A four-layer practice coil set, with upper layers shortened to enable viewing the lower coil ends, is shown in Figure 4. This multi-layer coil set takes advantage of a trick that while leads remain trapped with planar coils, ending the coil set with a Serpentine winding pair lets the leads be easily brought out. Such multi-layer combinations of different coil types we call Serpentine Planar Hybrid coil windings.

The final 1.6m Next Linear Collider (NLC) prototype winding, a three-layer coil set, is

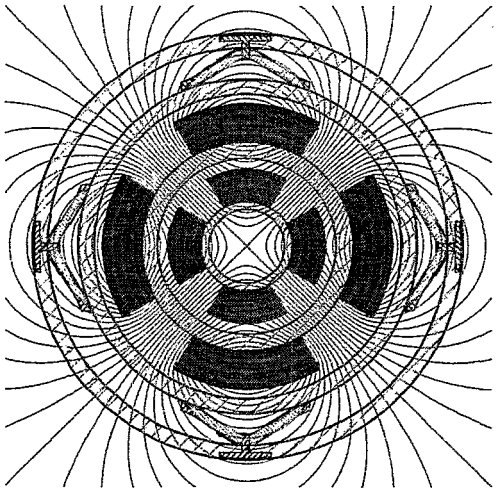


Figure 6. Revised QD0 design. Inner coil has four triple-layer coil sets for additional current margin.

shown in Figure 5. Its measured field harmonic content was much better than that required for a linear collider, and this result verified that the mid-point support was effective in limiting support tube flexure during coil winding.

Figure 6 shows a revised cross section for a multi-layer coil, using parameters from the 1.6 m prototype, to achieve the NLC design gradient 144 T/m with close to 20% current margin in a 3 T detector solenoidal field. An earlier design had about 10% current margin; however, recent test experience shows that first quench (i.e. result with no training) for BEPC-II multi-layer coils was 10% below the predicted short sample limit. The increase in margin with the new coil parameters is, therefore, quite significant.

In summary, during the course of this LDRD we learned that an original compact superconducting QD0 design was not practical and a simple fix would lead to an unacceptable decrease in performance, as measured in current margin, due to a decrease in coil packing efficiency. However, with invention of a new coil winding topology, we were able to recover sufficient margin to be able to satisfy the QD0 design requirements. We also demonstrated that a simple measure, adding a mid-point support, was adequate to deal with support tube flexure difficulties found when winding full length coils on such small diameter tubes.

Before start of work for this LDRD the baseline QD0 design called for a permanent magnet quadrupole. Since then the physics community has determined that it is important to have an adjustable strength QD0 so that energy scans can be performed. With this LDRD we have demonstrated the feasibility of constructing an adjustable QD0 that meets strength and space requirements. Since the time of the ITRP report the compact superconducting QD0 design is now the baseline design.

The Serpentine coil-winding concept that was invented during the course of this LDRD has completely changed the way we wind magnets. This innovation came along just in time to be incorporated into BEPC-II production and has already been used to make prototype correction coils for the Japan Proton Accelerator Research Complex (JPARC) project at KEK, the High Energy Accelerator Research Organization.
The production efficiency and coil design flexibility of Serpentine Planar Hybrid winding turned out to be critical in Fermilab's choice of BNL to make corrector magnets for the BTeV project. BTeV corrector production is a new, fairly major BNL Magnet Division project that will start up once BEPC-II production winds down. Without demonstrated capability to wind such unconventional coils, it is not clear if BNL would have been chosen.

SPECIFIC ACCOMPLISHMENTS:

KEK has adopted a variant of the Serpentine style corrector design for its JPARC corrector magnets. This smaller project takes place near the end of BEPC-II production and beginning of BTeV (reported on at MT18, see BNL-72205-2004-CP).

Serpentine winding is likely to play a roll in possible magnets for the eRHIC project (see C-A/AP/156 and V. Ptitsyn et. al. "eRHIC, A FUTURE ELECTRON-ION COLLIDER AT BNL," presented at EPAC'04) and a possible Super-B Factory Upgrade of PEP-II. It also inspired the Detector Integrated Dipole concept of Parker and Seryi (see MDN-637-40).

We anticipate presenting our final QD0 design option resulting from this LDRD at the PAC'05 Conference. Our preliminary compact QD0 design has been referred to by many presenters at more than eight US and international linear collider workshops and collaboration meetings (for a sampling from recent SLAC ILC meeting, see Dugan http://www-project.slac.stanford.edu/ilc/meetings/workshops/US-ILCWorkshop/talks/Dugan_USLCTOS.pdf, Seryi http://www-project.slac.stanford.edu/ilc/meetings/workshops/US-ILCWorkshop/talks/ILC_BDIR_Oct14.ppt and Parker http://www-project.slac.stanford.edu/ilc/meetings/workshops/US-ILCWorkshop/talks/SpecialMagnets1.pdf) and was incorporated into the final design report of the US Linear Collider Options Study (see Chapter 6, at URL: http://www.slac.stanford.edu/xorg/accelops/Full/LC_opts_full.pdf).

LDRD FUNDING:

FY 2003	$125,000
FY 2004	$129,829

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, coupling of numerical models of different scales. The success of the work will give BNL an edge in competing for funding in ongoing and future programs such as ARM, TAP, and Water Cycle Program.

APPROACH:

Two primary objectives in this fiscal year continue to be empirically examining the issue of the size distribution universality and seeking applications of the systems theory to cloud parameterizations. Analysis of observational data and theoretical studies were carried out to achieve these objectives. More data from aerosols, clouds, and rains were examined to substantiate our previous finding on the size distribution universalities using the approaches developed in last fiscal year. Especially, hailstone size distributions were analyzed as a new particle group. An entirely new type of parameterization of the autoconversion process was theoretically derived by coupling the systems theory with the size truncation function introduced to account for the effect of the size truncation of the cloud droplet size distribution.

TECHNICAL PROGRESS AND RESULTS:

In the last fiscal year, progress was made on two fronts. Briefly, 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. Size distributions belong to the universality of the second kind (hereafter second universality) if they statistically follow a common distribution family. Preliminary results indicated that particle size distributions generally do not exhibit the first universality, but respect the second universality. We also showed that size distributions are well described by the Weibull distribution expected from the systems theory. A new Kessler-type parameterization for the autoconversion rate was theoretically derived, which is given by

$$P=\kappa\left[\frac{\left(1+3\varepsilon^2\right)\left(1+4\varepsilon^2\right)\left(1+5\varepsilon^2\right)}{\left(1+\varepsilon^2\right)\left(1+2\varepsilon^2\right)}\right]N^{-1}L^3H\left(r_6-Rr\right), \quad (1)$$

$$r_c=5.6084\times10^2\left\{\left[\exp\left(\frac{3\times10^{-17}N}{L}\right)-1\right]\frac{1}{L}\right\}^{1/6}\approx0.99\left(\frac{N}{L^2}\right)^{1/6}, \quad (2)$$

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: (1) it is theoretically derived instead of being

empirically obtained, and therefore each term has clear physical meaning; (2) unlike the existing schemes, r_c has no empirical parameters that have to be arbitrarily tuned; (3) it explicitly accounts for the effect of the relative dispersion on the autoconversion rate, enabling us to quantify the influence of aerosol-enhanced dispersion on the evaluation of the second indirect aerosol effect.

In this fiscal year, new progress was made in the same areas that had been investigated in the last fiscal year. In the area of the size distribution universalities, more data from aerosols, clouds and rains were examined. Especially, hailstone size distributions were analyzed as a new particle group. The additional results basically support the previous findings. As shown in Fig. 1, particle size distributions generally do not follow the same normalized size distributions, suggesting that atmospheric particles, including hailstones, do not exhibit the first universality.

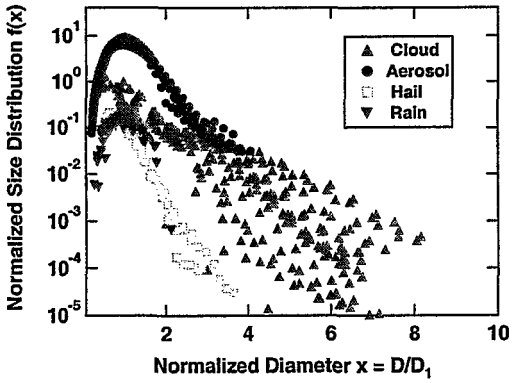


Figure 1. Illustration of the first universality. The additional data from aerosols, clouds, rains and hailstones further support the notion that atmospheric particles generally do not respect the first kind of the universality.

However, Figure 2 shows using the same data that atmospheric particles respect the second universality, even for the hailstone size distributions, and that the Weibull distribution well describes all data as expected from the systems theory.

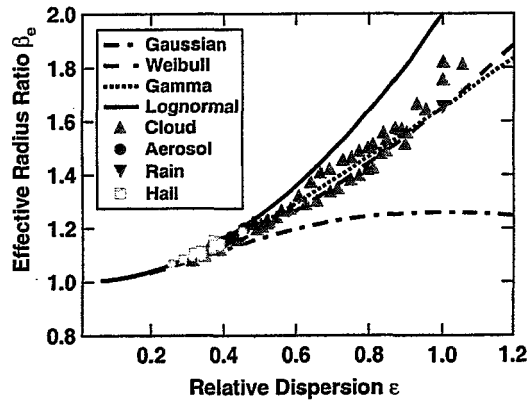


Figure 2 shows the same data presented in Fig. 1. Note that in the (ε, β_e) diagram, each point represents a size distribution. A collapse of the data points onto a specific $\beta_e(\varepsilon)$ curve suggests the second universality and the corresponding distribution function.

In the area of the cloud parameterization, we focused on improving the parameterization developed in the last fiscal year by considering the effect of the size truncation of the cloud droplet size distribution on the parameterization and eliminating the need to specify the driving radius, r_6, in the previous scheme. It is realized by generalizing our previous formulations. As a result, a new type of parameterization was derived that is entirely different from the existing parameterizations such as the Kessler-type and the Sundqvist- type. Briefly, it is given by

$$P=\left(\frac{3}{4\pi\rho}\right)^2\kappa\left[\frac{\left(1+3\varepsilon^2\right)\left(1+4\varepsilon^2\right)\left(1+5\varepsilon^2\right)}{\left(1+\varepsilon^2\right)\left(1+2\varepsilon^2\right)}\right]N^{-1}L^3T(x_c), \qquad (3a)$$

$$T(x_c)=\frac{1}{2}\left(x_c^2+2x_c+2\right)\left(1+x_c\right)e^{-2x_c}, \qquad (3b)$$

$$x_c=\frac{\rho_w\nu}{\kappa^{1/2}}\rho_{con}^{1/2}N^{3/2}L^{-2}=9.7\times10^{-17}N^{3/2}L^{-2} \qquad (3c)$$

The new parameterization not only provides theoretical explanations for, but also removes deficiencies of, the existing types of parameterizations. Especially, it provides more realistic representation of the transition from cloud droplets to raindrops than the discontinuous one of the Kessler-type parameterization. As an illustration, Fig. 3

offers some comparison of this new parameterization with our previous one.

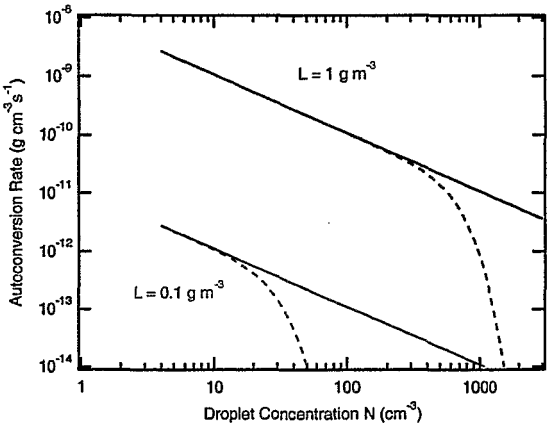


Figure 3. Comparison of the new parameterization (dashed) to our previous Kessler-type (solid). Note that in stead of smoothly falling off at some point of the new parameterization, the Kessler one will drop off discontinuously (not shown in the figure).

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 so far. The additional evidence that size distributions of atmospheric particles (including aerosols, clouds, rains, and hailstones) tend to follow the Weibull distribution lends further support to the fundamental principals on which the current systems theory is built. The new parameterization not only ends the common practice of arbitrarily tuning empirical parameters in climate models but also provides more realistic representation of the threshold behavior, and has the potential to improve all cloud-related models. Our previous parameterization has already been used to improve climate models.

SPECIFIC ACCOMPLISHMENTS:

Referred publications:

1. Y. Liu, P. H. Daum, and R. McGraw, 2004: A new analytical expression for the critical radius in the autoconversion parameterization. Geophys. Res. Lett., 31, L06121.

2. Y. Liu and P. H. Daum, 2004: Parameterization of the autoconversion process. Part I: Analytical formulation of the Kessler-type parameterizations. J. Atmos. Sci., 61, 1539-1548.

3. L. D. Rotstayn and Y. Liu, 2004: A smaller global estimate of the second indirect aerosol effect. Geophys. Res. Lett., (submitted).

4. Y. Liu, P. H. Daum, and R. McGraw, 2004: Size truncation effect, threshold representation and a new type of autoconversion parameterization. Geophys. Res. Lett., (submitted).

LDRD FUNDING:

FY 2003	$45,000
FY 2004	$45,447

Measurement of HO_2 Radicals by ChemiLuminescence Analysis of Atmospheric Radicals (CLAAR)

Stephen R. Springston *03-027*

PURPOSE:

The HO_2 radical is a key intermediate in the generation of atmospheric smog. Quantitative measurements of HO_2 over a wide range of ambient conditions are essential for validation of the chemical models used to predict pollution events and design remediation strategies. Existing analytical methods using laser-induced fluorescence are complex and not suited for broad deployment in monitoring networks.

We have developed a practical method for *in situ* monitoring that is suitable for widespread 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 these data from which processes can be deduced and models are tested. Our group in the Atmospheric Sciences Division has developed innovative techniques for measuring many species. Direct measurement of the HO_2 radical is challenging because of its low concentration and high reactivity.

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 HO_2 radicals by monitoring the resulting chemiluminescence with this reagent following collection of air samples into aqueous solution. The continuous collection of air samples is based on instrumentation developed at BNL for measuring atmospheric peroxides.

Implementation of this method has been carried out by Jun Zheng, a graduate student attending SUNY Stony Brook and working at BNL. This work has included assembly of instrumentation, liquid and gas-phase calibration methods and field deployment. The resulting instrumentation has the advantages of minimal weight, size and power consumption making it attractive for widespread deployment in monitoring networks and eventually aboard aircraft platforms. Field observations were interpreted with a one-dimensional photochemical model.

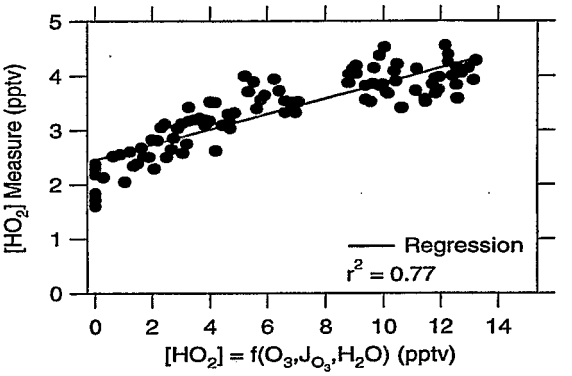
TECHNICAL PROGRESS AND RESULTS:

During the first year, a prototype instrument was constructed and response to liquid-phase HO_2 was demonstrated. Response sensitivity was ~0.7 pptv in air at 2-min resolution. These results confirmed the 'proof of concept.'

The primary aqueous HO_2 standards used for method development exhibit high accuracy but are only stable for a period of hours and require a calibrated ^{60}Co γ-irradiation facility. Therefore, we developed and evaluated a portable generator to produce a gas-phase transfer standard for field deployment. The gas-phase generator uses UV photolysis of water vapor in the presence of carbon monoxide under controlled conditions to generate gaseous HO_2 over a broad concentration range spanning ambient atmospheric levels. Unlike published methods using the same chemistry which depend on knowledge of photolysis cross section and radiation flux to calculate the

output concentration, our transfer standard is referenced to the accuracy of our 'primary' aqueous standard. Thus, uncertainties due to photolysis inhomogeneities and HO_2 wall losses are not important as long as they remain constant. We have found the reproducibility of the portable generator to be suitable for extended field deployment. Having a well-characterized gas-phase standard is essential for instrument evaluation. We have demonstrated unit collection efficiency of gas-phase HO_2 and monitored response stability during operation. Experimental measurements show wall losses are minimal under laboratory conditions. Tests of atmospheric interferences are ongoing.

We used a one-dimensional photolysis box model to evaluate the HO_2 observations from our initial instrument deployment at Whiteface Mountain, NY, in late summer of 2003. This site was chosen because the low concentrations of NO_x and anthropogenic hydrocarbons were expected to facilitate data interpretation. Thus, there are relatively few chemical species involved in HO_2 production, and the relevant set of rate equations can be solved analytically for the steady state HO_2 concentration. The results show the expected diurnal variation in HO_2, and the magnitude of the peak abundance at midday is consistent with calculated HO_2 concentration at other rural sites. Unfortunately, isoprene and formaldehyde were not measured at this site, and concentrations of these species are necessary for accurate computation of model HO_2. However, the results are reasonable. For example, during an observation period characterized by low concentration of NO_x, where we would expect O_3 photolysis to be the source of HO_2 and peroxide production the principal sink, the steady state concentration of HO_2 is a function of the ozone photolysis frequency and the concentrations of O_3 and H_2O. The figure below shows a good correlation between measured and modeled HO_2.



The systematic over prediction of HO_2 is due to several factors, including the deposition of HO_2, and the fact that our measurement does not capture organic peroxy radicals, RO_2, which are likely to represent a significant fraction of the calculated radicals.

During the coming year, we will continue development of this technique. A key element for airborne operation is positioning the sampling coil in the free air stream in order to eliminate transfer tubing. Testing will be done during research aircraft flights as they become available. Intercomparisons of this method with independent techniques at other institutions are being planned.

SPECIFIC ACCOMPLISHMENTS:

Non-Disclosure letter with Ocean Optics, Inc., Orlando, FL.

"Quantitative Determination of Atmospheric Hydroperoxyl Radical" patent applied for by Office of Intellectual Property and Sponsored Research, Brookhaven National Laboratory, 8/31/04.

Development of a Chemiluminescence Technique for Hydroperoxyl Radical (HO2) Measurement in the Troposphere, Jun Zheng, Ph.D. dissertation, Stony Brook University, in preparation.

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$ 99,045

Chemistry of the Rhizosphere

Mark Fuhrmann *03-030*

PURPOSE:

Reactions take place around plant roots on the scale of mm to microm 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 was 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.

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) increase plant uptake of a variety of contaminants including Pb and ^{241}Am [Fuhrmann and Lanzirotti, J. Env. Rad.]. However, it was 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 is the question to be addressed.

TECHNICAL PROGRESS AND RESULTS:

Some of the initial work for this LDRD project involved experimental follow-up of earlier field work on plant uptake of contaminants. Subsequently, we focused on two hyperaccumulators; *Thalspi 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. She has demonstrated that As, no matter what its original form, is reduced in the fern within several days and is maintained in that state in the living plant. Live leaf x-ray absorption near edge structure (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.

For the Zn plants, synchrotron based microprobe and microXANES were used to assess speciation and distributions of Zn in roots and shoots. At issue is if there are differences in how Zn enters roots of the two species, that is either along the length of the root or only at root tips. Figure 1, an X-ray fluorescence map done at X-26A at NSLS, shows that Zn rapidly enters the non-accumulator through the tip. The hyperaccumulator seems to develop high concentrations along the length of the root. We were also able to show that Zn is accumulated in a form that looks similar in XANES spectra, no matter what the original Zn compound in the soil was.

We have used infra-red 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. Uptake of Pb into plants, as an EDTA complex, is rapid and most of the complex remains intact as it is translocated to the shoots. However, a fraction of the Pb is dissociated from EDTA and accumulated in the stele of the root, apparently as sorbed Pb. Breaking the complex is likely the result of acidification in the stele. This was determined in collaboration with David Singer (a graduate student at Stanford U), A. Lanzirotti (U of Chicago), and Lisa Miller (NSLS). In this work we used a unique combination of synchrotron based tools; x-ray fluorescence (XRF) tomography and microbeam Fourier Transform Infrared (FTIR) spectroscopy mapping. Some of these results are illustrated in Figure 2, showing the distribution of total Pb in a tomographic cross-section of a root as well as the distribution of Pb-EDTA in a near-by section of the same root. Concentrations of total Pb in most, but not all, of the stele were comparable to those in the root cortex. However, no signal for Pb-EDTA was observed in any portion of the stele but was clearly present in the cortex.

Based on the success of the EDTA work, we attempted a very challenging search, using synchrotron based microbeam FTIR, for naturally produced complexing agents exuded by living plant roots. We believe that we have observed these materials as evaporated deposits on IR windows but we were unable to observe them in-situ.

SPECIFIC ACCOMPLISHMENTS:

M. Fuhrmann, M. Lasat, S. Ebbs, J. Cornish, and L. Kochian, Uptake and Release of ^{137}Cs by Five Plant Species as Influenced by Soil Amendments in Field Experiments, *Journal of Environmental Quality*, 32:2272-2279, 2003.

M. Fuhrmann and A. Lanzirotti, Radionuclide Uptake by Tobacco as Influenced by Application of Chelators to Soil, accepted with revisions, *Journal of Environmental Radioactivity*, 2004.

M. Fuhrmann, D. Singer, A. Lanzirotti, and L. Miller, Fate and Distribution of Metal-EDTA Complexes During Plant Uptake, *Submitted to Environmental Science and Technology*, 2004.

M. Fuhrmann, N. Warchola, D. Singer, and T. Smith, Uptake of RCRA elements and Radionuclides by Plants in Filterbeds of a Sewage Treatment Plant. In Preparation.

M. Kissell, R. Reeder, and M. Fuhrmann, Uptake of arsenic by Pteris ceritica: 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	$101,573

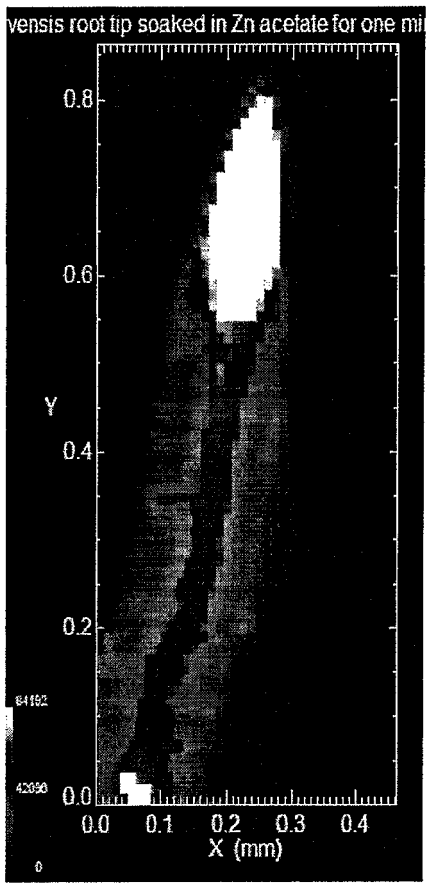
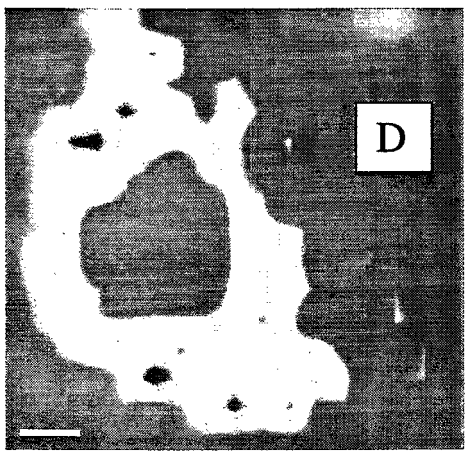
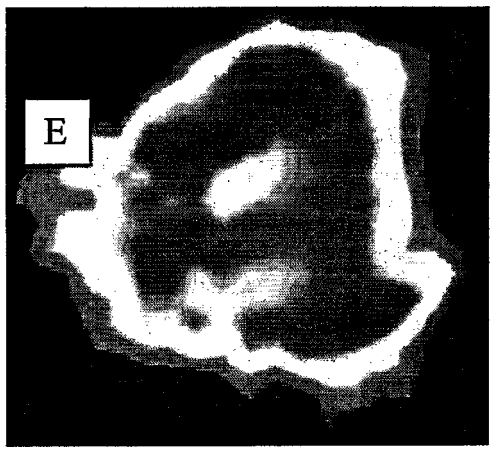
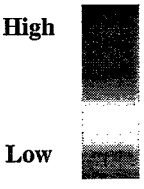


Figure 1. T. arvensis root tip after soaking in 2mM Zn acetate solution for 1 minute and then rinsed in DIW. Step size = 12um. Time = 6 sec/pixel NSLS X-26a







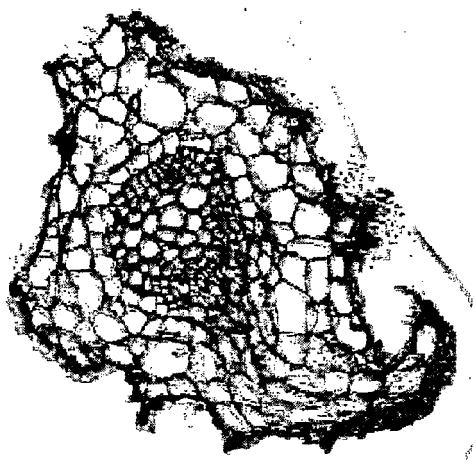


Figure 2. Microbeam FTIR map of Pb-EDTA signal (D), microbeam XRF Tomographic map of Pb distribution (E), and Photograph of Tagetes root exposed to Pb-EDTA.

Integrated Analysis of Carbon and Nitrogen Metabolism in Plants and Subsequent Analysis of Photosynthetic Acclimation to Growth in Elevated pCO_2

Alistair Rogers *03-039*

PURPOSE:

The objective of this project was 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 OBER.

APPROACH:

A sustained, and maximal, stimulation of photosynthesis and growth in future partial pressures of carbon dioxide (pCO_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 pCO_2. Currently, there is a gap in the scientific understanding of how carbon and nitrogen metabolism interact at elevated pCO_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 pCO_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 pCO_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 respectively, their Free-Air CO_2 Enrichment facilities at the University of Illinois at Urbana Champaign (SoyFACE) and their Harshaw Experimental Forest, Rhinelander, WI (Aspen FACE).

TECHNICAL PROGRESS AND RESULTS:

Progress in FY 2003

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.

Analyses of the first year of field data from the SoyFACE experiment showed that soybeans grown at elevated pCO_2 had a reduced leaf nitrogen content. 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 pCO_2. It is hypothesized that plants grown

at elevated pCO_2 were better able to utilize an increased supply of ureides from *Rhizobia* because the excess photosynthate produced at elevated pCO_2 provided the carbon skeletons necessary for amino acid biosynthesis.

Progress in FY 2004

Field work continued at the SoyFACE experiment and also at the AspenFACE and PopFACE experiments. Data from the SoyFACE field site show the same pattern as that from FY 2003 and a manuscript is in preparation. Experimental analysis of FY 2004 data from AspenFACE and PopFACE is complete and will be presented at an AspenFACE meeting in December. Collaboration with Dr. Leakey (UIUC) on research conducted at the Biosphere II experiment has resulted in the preparation of a second manuscript and Dr. Rogers is also preparing a book chapter resulting in part from research conducted during this LDRD.

SPECIFIC ACCOMPLISHMENTS:

In collaboration with ORNL and LANL Dr. Rogers has submitted a proposal in answer to an RFP from the *Program for Ecosystem Research* (BER). If successful this proposal would bring $700K to BNL. (HERMES: Hierarchical Experimental Responses at Macromolecular to Ecosystem Scales. $5.3M)

Presentations

Poster: *American Society of Plant Biologist, Honolulu, HW.* 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. Jul. 25-30, 2003

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. Oct. 16-17, 2003

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. Nov. 3-6, 2003

Talk: *Ecological Society of America, Tucson, AZ.* Leakey, A.D.B.; 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 [CO_2]. Aug. 4-8, 2003

Invited Talk: *International Photosynthesis Congress, Montreal, Canada.* Rogers, A. The response of plant carbohydrates to elevated CO_2. What have we learnt from FACE studies? Aug. 29 – Sept. 3, 2004

Invited Talk: *International FACE workshop, Monte Verità, Ascona, Switzerland.* Rogers, A. Rules and their exceptions in the response of plant carbohydrates to elevated CO_2. Mar. 20-25, 2004

Publications

In Prep: 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. (FY 2003 results).

In Prep: Leakey, A.D.B.; 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 [CO_2]. (FY 2003 results).

In Prep: Rogers, A.; Ainsworth, E.A. (2005) The response of foliar carbohydrates to elevated [CO_2]. In: Short and Long term effects of elevated atmospheric CO_2 on managed ecosystems (eds J. Nösberger, S.P. Long, G. Hendrey, C. van Kessel, M. Stitt), Springer.

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	$67,283

Evaluation of High-Energy Radiation Effects in Materials

George A. Greene *03-050*

PURPOSE:

The purpose of this LDRD was 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 at cryogenic conditions. 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. The objective of this work was to develop a small-scale radiation-effects apparatus that is free of major infrastructure requirements, portable, inexpensive to operate, and capable of measuring a wide variety of radiation effects in materials due to high-energy protons and heavy ions. Some of the radiation effects that were investigated include radiation damage and energy deposition in metals due to irradiation by high-energy protons.

APPROACH:

Recently, applications of radiation effects to particle accelerators have risen in prominence with the introduction of facilities such as the AGS-RHIC-NSRL at BNL, LANSCE-PRAD at LANL, SNS at ORNL, and LHC at CERN, to name a few. Projects on the drawing board such as Muon Collider, Neutrino Factory, MECO/KOPIO, and RIA promise to motivate investigators to pursue additional studies into materials behavior and radiation effects previously overlooked, such as shielding against galactic cosmic rays and transmutation of advanced reactor fuels. Computational tools for radiation effects could benefit from the availability of experimental data for model development and validation. 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. This LDRD was intended to develop and demonstrate a small, portable and versatile vacuum-cryostat radiation-effects apparatus.

TECHNICAL PROGRESS AND RESULTS:

FY 2003 Results:

The vacuum-cryostat apparatus was completed and successfully tested at 3 K and 5×10^{-9} Torr. A general-purpose data acquisition system was assembled with Keithley components that operates on a computer-controlled platform called Test Point. General-purpose data acquisition and control software was developed to provide an interactive interface with the experimental hardware. Accurate and high-precision measurements of voltage, current, and resistance were made of a variety of test objects and transducers through a remote instrumentation interface. Cryogenic temperature measurements as well as cryogenic measurements of the resistance of radiation damage targets were made to verify the accuracy and precision of the measurement system at liquid helium temperatures. The assembled and operational radiation-effects apparatus that

was constructed for these measurements is shown in Figure 1 below.

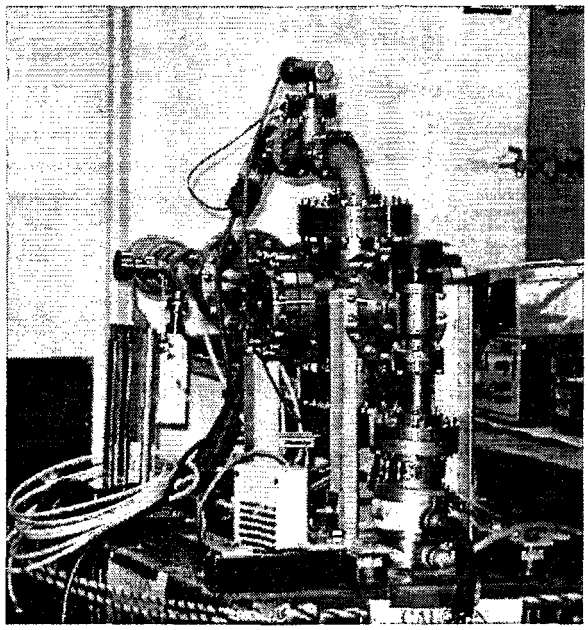


Figure 1. Radiation effects apparatus.

FY 2004 Results:

Experiments were conducted to measure energy deposition and radiation damage effects in metals due to proton irradiation. Energy deposition measurements were made downstream of a proton spallation target in order to measure the magnitude of the temperature spike that a superconducting magnet would experience due to scattered radiation from an upstream target. The data were precise and reproducible, and indicated that the energy deposition due to scattered radiation from an upstream high-Z target would be sufficient to cause a superconducting magnet to quench if sufficient shielding were not provided for the magnet. A generalized correlation of the data was developed for the analysis of thermal spike effects in a LHe-cooled cold mass due to scattered radiation from an upstream tungsten spallation target, as shown in Figure 2.

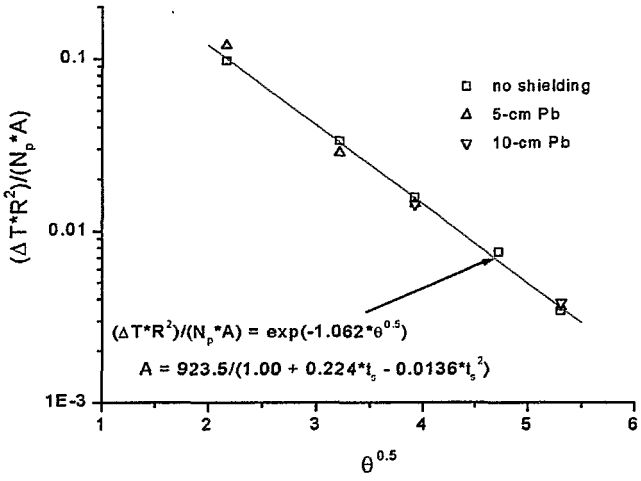


Figure 2. Generalized energy deposition correlation [1,2].

Other experiments were conducted to measure the radiation-damage displacement cross sections in structural metals due to irradiation by high-energy protons. The metals studied were copper and tungsten, candidate materials for AFCI (Advanced Fuel Cycle Initiative) and Rare Isotope Accelerators components, and the proton energies studied were 1.10 GeV and 1.94 GeV. Extremely accurate, precise, and reproducible resistance measurements were conducted of radiation-damage wire harps at LHe-temperatures, both before and after proton irradiation, to measure the resistance implanted in the targets due to the production of defects in the wires. These resistance increments were related to the displacement cross sections for both metals at both proton energies tested through defect-density data, and were compared to predictions by the MCNPX computer code as shown in Table 1.

Table 1. Measured vs. calculated displacement cross sections for copper and tungsten [3,4].

Metal	Proton Energy	$\sigma_{d,measured}$	$\sigma_{d,calculated}$
	(GeV)	(barn)	(barn)
Cu	1.94	1820	2400
	1.10	1485	2750
W	1.94	7840	9070
	1.10	4970	8230

SPECIFIC ACCOMPLISHMENTS:

Publications:

1. Greene, G. A., et al., "Measurements of the Specific Heat of High-Purity Copper at Temperatures Below 8 K by a Modified Pulse-Heating Technique," Int. J. Exp. Thermal and Fluid Science (2003).

2. Greene, G. A., et al., "Energy Deposition in a Thin Copper Target Downstream and Off-Axis of a Proton-Radiography Target," Nucl. Instr. and Meth. B (2003).

3. Greene, G. A., et al., "Direct Measurements of Displacement Cross Sections in Copper and Tungsten by 1.10-GeV and 1.94-GeV Protons at 4.7 K," AccAppN03, San Diego, CA (2004).

4. Greene, G. A., et al., "Direct Measurements of Displacement Cross Sections in Copper and Tungsten Under Irradiation by 1.10-GeV and 1.94-GeV Protons at 4.7 K," submitted for publication to J. Nuclear Materials (2005).

Future Funding:

DOE-Office of Nuclear Energy, AFCI Program: Project in Transmutation Engineering funded in FY05, $240K received. Project in Fuels Development expected in 2nd quarter-FY05, $300K expected.

DOE-Office of Science, Rare Isotope Accelerator Program: Proposal submitted to DOE-OS-Nuclear Physics to measure radiation effects in RIA, $300K proposed.

NASA-Office of Biological and Physical Research: Proposal submitted to NASA for FY04 funding to use this apparatus at NSRL for shielding evaluation, $250K proposed.

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$105,354

Structural Properties of Methane Hydrates

Devinder Mahajan *03-056*

PURPOSE:

The global abundance of methane hydrate, a high-content (~15 wt%) methane source, makes it a promising future energy source. The key to recovering methane from hydrates is to understand the precise conditions of their kinetic stability in host sediments. Specifically, an uncertainty remains as to the nature of sediment pores in which methane hydrates prefer to form and reside. The purpose of this project was to measure key physical properties of host sediments from methane hydrate sites and then correlate their structural characteristics with the formation of guest (methane hydrate)-host (sediment) complexes.

APPROACH:

Our approach involved: 1) measuring porosity and related properties of the sediment samples, obtained from the methane hydrate sites, using Computed Microtomography (CMT) and 2) obtain baseline methane hydrate formation/ decomposition data on the guest-host complexes in the characterized sediments. To achieve our objectives, collaborations were 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 instruments to measure complementary methane hydrate properties and 2) Dr. K. Jones (BNL) to measure porosity and related properties of the host sediments at Beamline X27A at the NSLS. In addition, a BNL Methane Hydrate Unit has been set up to mimic subsurface conditions that are native to methane hydrate.

TECHNICAL PROGRESS AND RESULTS:

Three sediment samples: two from Blake Ridge, off the coast of the Carolinas (depths of 50 m and 667 m), and one from Georges Bank (0.2 m), both well-established methane hydrate sites, were obtained though USGS to establish their porosity differential as a function of depth. The CMT technique was used to collect 2-D data on the sediment slices, from which 3-D images of the sediments were reconstructed (Figure1).

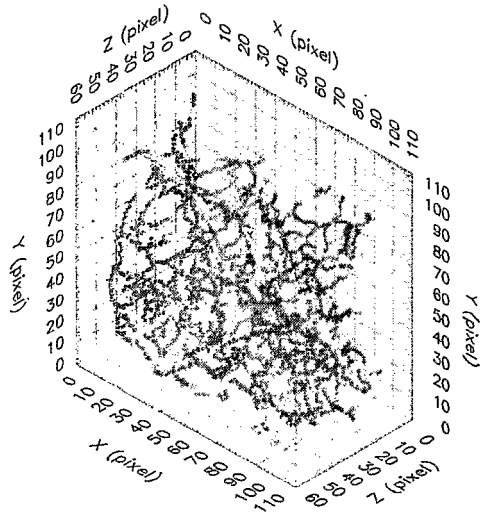


Figure 1. Fluid flow pathways reconstructed from the 2-D data for the 50 meters depth sample. Small diameter pathways correspond to a red color whereas a blue color indicates larger diameter pathways. The pixel sizes for the three axes are .0068 mm.

The calculated porosity values show that sediment porosity decreases as a function of depth: 80.7%, 64.3%, and 58.1% for 0.2, 50 and 667 meters samples respectively. Further data refinement now continues. In addition, a customized cell, capable of operating at high pressures and low temperatures (those mimicking ocean floor conditions), was obtained from a vendor to study *in situ* methane hydrate formation at the beam line.

A parallel effort was initiated to study the methane hydrates formation/decomposition

in the characterized sediments. A unit, previously used for gas and oil research, was modified and baseline kinetic data of pure methane hydrate formation were collected. The data fits well with the reported literature studies (Figure 2).

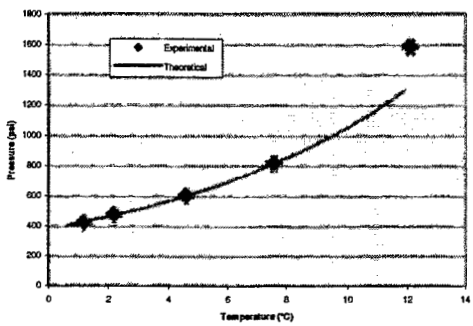


Figure 2. Pure methane hydrates formation in the BNL unit. The line represents theoretical values.

Further work to establish the effect of sediment porosity on methane hydrate formation kinetics is in progress.

SPECIFIC ACCOMPLISHMENTS:

Refereed Publications

1. Mapping Metal Catalysts Using Synchrotron Computed Microtomography (CMT) and Micro X-ray Fluorescence (μXRF). K. W. Jones, H. Feng, L. Lanzirotti, and D. Mahajan. Topics In Catal. In Press.

2. Fundamental Challenges to Methane Recovery from Gas Hydrates. P. Servio, M. Eaton, D. Mahajan, and W.J. Winters. Topics In Catal. In Press.

3. 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 press.

Presentations

- "Technical Challenges to Mining Methane Hydrates: The next Energy Frontier". Marine Sciences and Atmospheric Sciences Colloquium Series, Stony Brook University, New York. February 6, 2004.

- Gulf of Mexico Naturally Occurring Gas Hydrates JIP Workshops. Denver. CO. 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 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 Micro tomography (CMT). D. Mahajan, K. W. Jones, H. Feng, and W. J. Winters. Presented at the Symposium on Gas Hydrates, 2003 AICHE 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	$103,647
FY 2005 (budgeted)	$ 15,000

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 seek a research position within the wind energy community.

APPROACH:

This program has two components: (a) structural dynamics and (b) materials engineering of turbine-tower-foundation systems. Relevant descriptions for each follow.

(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 the methodology using the Compaq Visual Fortran was undertaken. Pavan Vaddadi, a Ph.D student from Stony Brook University, is a collaborator with respect to computer implementation.

(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 CO_2-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:

In this project we developed mathematical models of wind turbine systems on the basis of elastodynamic theory. The analysis was done 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, we investigated a variety of solution techniques. Specifically, solutions were obtained by 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 considered eigenvalue solutions of the associated fixed-base system. In addition, efforts were spent to automate portions of the required input-output data, graphics and pre and post processing. Finally, we worked on some benchmarking and verification problems, using simple models with few degrees-of-freedom.

With regard to the material investigations, a series of three sustainable concrete mixes and one control mix has been designed and a series of material testing was pursued. 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.

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 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 were prepared and subsequently subjected to 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 fibres is being studied, along with any degradation of the concrete. These tests indicate that only fibres close to the exposed surface are susceptible to corrosion. Other durability tests were carried out 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 was completed. The durability tests provide a comparative evaluation of the performance of the materials in seawater and deleterious groundwater conditions. Finally, a variety of other material tests were performed which include determination of elastic and thermal properties for use in the modeling component.

SPECIFIC ACCOMPLISHMENTS:

Presentation and abstract, "Dynamics of Wind Turbine Systems," Philippacopoulos, A.J.; Berndt, M.L. for American Wind Energy Association Windpower 2003 Conference in Austin, TX, May 2003

Publication: "Sustainable Concrete for Wind Turbine Foundations," Berndt, M.B., submitted and accepted to the Journal of Materials Engineering, March 2004

LDRD FUNDING:

FY 2003	$140,000
FY 2004	$145,957

Investigation of Neutron and Gamma Probes to Detect Explosives in Sealed Containers

Michael Todosow *03-064*
L. Wielopolski

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. As a result of interest by the Department of Homeland Security in the detection of Special Nuclear Materials (SNM), issues associated with this application have also been addressed.

APPROACH:

It is proposed to use modern Monte Carlo methods (specifically the MCNP/MCNPX codes developed by Los Alamos National Laboratory) 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 detect explosives. However, because neutrons will activate materials, the focus is 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 was to evaluate the adequacy of the basic cross section data needed to evaluate this approach. The use of high-energy, mono-energetic gammas to detect SNM is also being explored. Based on the results of the initial survey phase, additional analyses will be performed to define the characteristics of a reference system(s) which might be based on neutrons only, gammas only, or a combination. Initial experiments needed 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.), will be identified.

TECHNICAL PROGRESS AND RESULTS:

The list of accomplishments for FY04 includes:

Target (I. Dioszegi, H. Ludewig, N. Simos, L. Wielopolski).

Part of our efforts in the past year was to provide a working target for a possible GRT. In support of this goal, we tested (in collaboration with CAD technicians) the existing Carbon-13 target. The target is in working condition, the chamber is vacuum tight, and the mechanical (rotating) parts are also in fair condition.

In addition, initial analyses of the thermal/ mechanical performance of candidate target options have been performed. Both ceramics (e.g., boron carbide), and metals (lithium) are being considered as possible target materials. The ceramic targets are generally characterized by a low Poisson ratio, a high Young's modulus, and a thermal expansion coefficient that is lower than that of candidate metallic substrates (copper and aluminum). Preliminary analyses have shown that the thermal gradients in the target/substrate arrangement lead to differential thermal expansion and thus a thermally induced bending stress in the target (ceramic layer). This stress will be the limiting factor in determining the beam spot size and power and eventually in the concept performance. In the case of metallic targets (lithium), the target will clearly be liquid (low melting point). In this case an understanding of the target dynamics will be required. A previous design developed for the BNCT program will be used as a starting point for this work.

Monte Carlo Simulations (I. Dioszegi, M. Todosow, and L. Wielopolski)

Simulations of a large-scale setup containing a 4' by 4' container (simplified as a large cylinder in the calculations) have been performed assuming a point source of 9.17225-MeV γ-rays and an array of 81 Barium Fluoride detectors arranged in arc geometry. Implementation of the parallel-processing version of MCNP with 3 fast processors have remarkably shortened the computation time for this large setup.

The computed results show that the method is sensitive for explosives with thicknesses down to about 2-cm., and that by rotating the container a relatively thin explosive sheet becomes well detectable when the container is rotated to the proper angle, in the simulated case to 90°. Besides the rotating setup we also simulated the gradual transfer of the container in front of the detector array.

Monte Carlo Simulations for SNM (M. Todosow, A. Mallen, G. Raitses)

M. Todosow is currently serving as a member of the DHS Active Interrogation Working Group (AIWG). In connection with this activity the ability of a system based on high-energy, mono-energetic gammas to detect SNM hidden in a large shipping container has been considered. Several container configurations defined by the AIWG have been simulated.

In FY05 the plan is to address the following issues:

- Consider the engineering and nuclear issues involved in the design of targets for producing mono-energetic gammas. Ideally, this will require data for the production of gamma rays via the interaction of protons with the target.
- Define the characteristics and conduct of operations of an integrated system for explosives detection and for SNM detection.
- Define RD&D needs for further development if warranted.

SPECIFIC ACCOMPLISHMENTS:

Presentations

L. Wielopolski, M. Todosow, J. Jones, **"CERBERUS: A Triple-Prong System for Inspecting Cargo Containers for IND, SNM, and Explosives,"** Active Interrogation Workshop, Idaho Falls, June 2004.

L. Wielopolski, M. Todosow, H. Ludewig, N. Simos, **"Production of Monoenergetic Gamma Rays for Cargo Container Inspection,"** CAARI-2004, October 2004. (accepted, but not presented due to LW illness).

Proposals

- Joint ANL-BNL-LLNL White Paper to DHS – "Combined Cargo Interrogation with Neutrons And High-Energy Mono-Energetic Photons"
- Radiological/Nuclear Countermeasures Program Proposal, Multi-Scanning System for Large Cargo Containers Inspection for SNM and Explosives Detection (submitted to DHS)
- "Analyses to Support Development of Advance Neutron and Gamma-Ray Detectors" (submitted to DOE/NA-22)

LDRD FUNDING:

FY 2003	$110,000
FY 2004	$112,370
FY 2005 (budgeted)	$ 92,000

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 non-destructive inspection method for monitoring the condition of electric cable insulation. The technique can detect many types of cable insulation damage that are not readily detectable using condition monitoring methods currently available. Benefits of this technique are: it is fast, it does not require de-termination of a tested cable, and it 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 in support of license renewal and nuclear plant life extension initiatives. This work advances BNL's Nuclear Safety/Regulation strategic initiative by involving the laboratory in developmental research for next-generation advanced reactor designs and their support technologies. The Federal Aviation Administration (FAA) and the National Aeronautics and Space Administration (NASA) are also committed to the development of new techniques that can provide a more accurate assessment of the condition of aircraft and spacecraft wiring insulation.

APPROACH:

Since 1994, BNL has served as the lead laboratory for the NRC Office of Nuclear Regulatory Research in a research program to study the service aging of electric cables in nuclear power plants and evaluate techniques for measuring and monitoring cable insulation degradation. Several technical journals had reported on a technique that used ultrasonic stimulation coupled with infrared imaging to identify defects in ceramics, cast and forged metal parts, and certain types of polymers. When stimulated by ultrasound, frictional heating caused by differential vibration of crack faces can be detected by infrared imaging. The types of defects that can be detected in this way resembled the aging-related damage and degradation in polymeric cable insulation that we have observed in our research with the NRC. Consequently, we proposed this research to study the application of the ultrasonic stimulation with infrared imaging technique for condition monitoring of electric cables.

The testing apparatus consisted of a 250W, 20 kHz, moveable ultrasonic head assembly mounted on a test platform. The ultrasonic horn was moved into contact with the test cable by a pneumatically operated actuator. A cooled digital infrared camera observed the stimulated cable and captured the image data. Control software implemented data display and accepted operator input to control and synchronize operation of the pneumatic actuator, the ultrasonic source, and the infrared camera. Ultrasonic output power, pulse duration, imaging parameters, and data acquisition parameters could all be controlled independently.

Typical nuclear power plant and aircraft cable specimens were irradiated and/or

thermally aged to simulate 20, 40, or 60 years of in-service aging. A range of cable sizes, constructions, and polymer insulating materials were prepared for testing. The test program evaluated the effectiveness of the technique for inspection of various insulation and jacket materials, different cable sizes, and a range of service aging. The best combinations of ultrasonic power level and contact pressure, ultrasound stimulation duration, data acquisition time, ultrasound application point, and infrared imaging location for each cable type or material were identified. Imaging data from each test run were manually processed to highlight the significant features contained in the data. Insulation and jacket material damage detection thresholds were determined. Limitations on ultrasound power level and pulse durations were identified.

TECHNICAL PROGRESS & RESULTS:

The ultrasound stimulation with infrared imaging testing program was completed in FY 2004. More than 30 different cables of varying sizes and service ages were tested. The ultrasonic probe, applied perpendicular to the surface of the cable insulation or copper conductors, successfully stimulated the cable insulation sufficiently to permit infrared imaging as far as 24 inches from the point of application.

Figure 1 - Infrared thermogram display indicating damaged electric cable insulation

Figure 1 is an example of an infrared imaging thermogram from one of the test runs that shows how frictional heating at hairline cracks in the insulation of an aged nuclear plant cable specimen glow when observed in the infrared.

Test data are being reduced, consolidated, and analyzed. Damage detection thresholds using ultrasound stimulation with infrared imaging are being correlated to degradation levels established by other polymer testing techniques, such as elongation-at-break.

In conclusion, the test program demonstrated that ultrasound with infrared imaging shows good promise as a useful cable condition monitoring technique and it is worthwhile to continue this research. The LDRD test data gathered will allow us to actively seek research funding from outside sponsors.

SPECIFIC ACCOMPLISHMENTS:

A final report is being prepared summarizing observations, test data, limitations, and recommendations for hardware modifications and procedures to adapt the technique for in situ testing. We will pursue patenting the idea of applying this technique to cable insulation inspection and condition monitoring. We are actively seeking further research funding from sponsors such as NRC, NASA, and FAA.

LDRD FUNDING:

FY 2003	$63,000
FY 2004	$74,604

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 for legitimate commercial applications. Background suppression technology coupled with high-resolution gamma-ray spectrometry can detect radiation near background levels and reduce false alarms by distinguishing materials with legitimate commercial or medical applications from material intended for malevolent use. This work demonstrated that background reduction technology combined with high-resolution gamma-ray spectrometry could be used outside the laboratory under field conditions for two different objectives. One objective was field identification of radiation signatures in small environmental-monitoring samples without sending the samples to a specialized laboratory for analysis. A second objective was 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.

APPROACH:

In FY 2003, we undertook a threefold approach, drawing on assets that were available at BNL. 1. A Compton suppression gamma-ray spectrometer in the Chemistry Department was used to establish the conditions for obtaining spectra of materials of counterterrorism interest with the greatest sensitivity and lowest background. This instrument had a germanium well detector surrounded by a Compton shield made of sodium iodide and was particularly suitable for analyzing small samples containing traces of materials of interest. This instrument established the potential usefulness of background suppression techniques in combination with a high-resolution well counter for counterterrorism applications and established the design basis for a portable instrument equipped with modern miniaturized electronics and a physically more robust shield made of bismuth germanate (BGO). 2. A simple method for separating the radium fraction from any one of four uranium decay chains was planned 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 explored the utilization and adaptation of a commercially available instrument, the Canberra ISOCS gamma-ray spectrometry system for counterterrorism purposes. Although it was developed for use in the decontamination and decommissioning of facilities, it could be modified to analyze and interpret spectra obtained from isotopes of interest in the counterterrorism area. BNL had two of these systems. We used the ISOCS for evaluation of the lighter, more portable Compton-suppression instrumentation that we planned to develop.

TECHNICAL PROGRESS AND RESULTS:

In FY 2003, we completed the Employment Safety Review (ESR) (1.3.5) process so that the necessary radioactive materials could be used with the various instruments. The Compton-suppression gamma-ray well-counter was refurbished and put back into operation. This included evaluation and adjustment of the photomultiplier tubes on the Compton shield and evaluation of the HPGe well counter and timing circuits. We recorded many spectra and reestablished the complex efficiency vs. energy curve and fitted it mathematically to calculate unknown values. (We acknowledge assistance from David Alburger in restoring the system to working order and of Kathy Kolsky for preparing quantitative radioactive multi-isotope standards for use in calibrating 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 materials containing natural radioactivity that are commonly shipped commercially and might obscure the presence of special nuclear materials.

Supplies for micro chemical separation of radium isotopes were acquired, and the separation procedure was tested. Further work involving separation of radium isotopes from uranium samples was deferred since a modern HPGe well counter made of low-background materials would have been needed to demonstrate the ultimate sensitivity of this method. This work could be revived on short notice.

In FY 2004, we acquired a Compton-suppression shield made of BGO and equipped with miniature photomultiplier tubes. We configured the BGO shield so that it could be mounted on a single support platform with any of several available hand-held HPGe detectors equipped with portable cryostats. We also acquired a modern miniature multi-channel analyzer (manufactured by Canberra) and had it equipped to our specifications with veto circuitry that would support use of the active Compton suppression shield with HPGe detectors of various types. Instrumentation Division has begun the design and construction of circuitry for integration of miniaturized high-voltage power supplies for the BGO crystals that will optimize the portability of the integrated Compton-suppression spectrometer. A small notebook computer was also acquired to support acquisition and analysis of high-resolution spectra with the Compton-suppression system; however, the smallest and lightest, and therefore the most appropriate computer for this application was not obtained because of cost and available funds. Appropriate software implementing an ANSI standard for counterterrorism use by personnel without extensive technical training was also acquired. The integrated system, including cryogenically cooled HPGe detector, weighs less than 50 lb (23 kg). Together, it convincingly demonstrates that a Compton-suppression spectrometer can be made portable and suitable for non-laboratory or field use in counterterrorism applications. However, further adaptation for field use in extreme weather conditions is still required.

To test the capabilities of the Compton suppression system and as an exercise in studying possible field uses of the new detector, we acquired four plutonium nitrate specimens (100 micrograms each) having differing isotopic compositions. The Institute for Reference Materials and Measurements (IRMM) at Geel, Belgium, prepared and characterized these materials for a multi-laboratory blind examination. We have measured spectra of all the plutonium samples using the rejuvenated

Compton-suppression germanium-well spectrometer in the Chemistry Department. However, analysis of the data remains to be completed. When we submit our final results, IRMM will provide certified values for the plutonium composition so that these samples will be available to BNL as certified reference materials for future work.

With the BGO shield, background suppression is accomplished in four ways. 1. Compton background outside the full energy peak is suppressed for Compton-scattering events when energy is deposited in both the BGO shield and in the HPGe detector. 2. The BGO shield serves as a collimator, providing directional orientation helpful in locating gamma-emitting items, without use of heavy-metal collimation and shielding. 3. The BGO shield provides passive shielding by absorbing background radiation. 4. The BGO serves as an active shield when a radiation event, e.g., a cosmic ray, deposits energy in both the BGO and the HPGe.

With the Compton-suppression HPGe well-detector configuration, we have demonstrated capability to detect 50 ng of ^{235}U or less than a microgram of plutonium contained in the material placed in the well. Results of this sensitivity would be available immediately without the delays that could be associated with sending samples to a specialized laboratory, although the Compton-suppression system might be used to screen and select promising environmental samples for more microscopic examination in the laboratory.

With a standard HPGe detector equipped with the active Compton-suppression shield, we have demonstrated that the background in spectral regions of interest in counterterrorism applications can be suppressed by a factor of 2 to 3, and further optimization appears possible. This increases the sensitivity for detection and correct identification of near background-level gamma-ray peaks for counterterrorism applications.

Two of the three investigators in this project are retired, and all three will continue to contribute their own time in FY 2005 to the following activities even if direct funding is unavailable: analysis of spectra to determine the composition of the plutonium reference samples; use of the integrated Compton-suppression spectrometer to measure materials assembled, e.g., in connection with the RADTEC project and to compare capabilities with other instruments tested at RADTEC. Instrumentation Division will complete the design and construction of circuits needed to support the Compton-suppression system and integrate it with the computer-controlled commercial data-acquisition and analysis system.

SPECIFIC ACCOMPLISHMENTS:

Unrefereed External Publications:

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.

A System for the Rapid Analysis and Interpretation of the Gamma Rays from Nuclear Materials after Their Initial Detection, Kane, W.; Lemley, J.; and Harbottle, G.; Institute of Nuclear Materials Management 45th Annual Meeting, Orlando, FL, July 18-22, 2004.

LDRD FUNDING:

FY 2003	$125,000
FY 2004	$134,174

Real-Time Consequence Assessment System for Atmospheric Terrorist Events in the Northeast Urban Corridor

R. Michael Reynolds *03-077*

PURPOSE:

BNL, in collaboration with the Department of Energy's Environmental Measurements Laboratory (EML) in Manhattan, began a long-term, urban meteorological measurement program in the vicinity of King and Varick streets in the West Village section of New York City. Early in 2003 three turbulence measuring sonic anemometer stations were deployed on the EML building and in the adjacent King Street Canyon. Later, in July, a borrowed Sound Detection and Ranging (SODAR) system was deployed on the EML roof. Scientifically, these measurements have produced a highly unique data set. This data set will provide extremely useful information on seasonal variations in the circulations above the city, over the rooftop, and in the canyon. This program has established BNL as a leader in homeland security research. This study has given BNL an important presence in NYC and has led to funding from the Department of Homeland Security (DHS) Urban Dispersion Program (UDP).

APPROACH:

The approach followed in this program has to pay attention to the dual goals of the effort: (1) to demonstrate ability to make long-term meteorological measurements in Manhattan, and (2) to become recognized as the leader in developing the tools needed for emergency response in the event of a sudden release of contaminants into the urban atmosphere. We formed a scientific team with the leading urban scientists in the country. The two lead consulting scientists are Robert Bornstein, San Jose State University, and Steve Hanna, Harvard. We continued the collaborative partnership with Bruce Hicks, NOAA Air Resources Laboratory, and Sam Lee, Environmental Measurements Laboratory.

TECHNICAL PROGRESS AND RESULTS:

The three sonic anemometer systems on the rooftop and sides of the EML building continued to operate until July 2004. At the start of 2004, a fourth sonic anemometer was added near street level in the King Street Canyon in order to better define the circulations there. This system was removed when the others came down in July. The street level canyon included temperature and relative humidity sensors. Each of the four sonic anemometer instruments produced 48 MB per day. The entire data set of approximately 25 GB is stored on a server in our laboratory and is backed up on a separate hard disk. 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.

The SODAR likewise provided an excellent look at the winds well above the building. We left the SODAR operating until the end of October so that we would have a complete year-plus data record (it was installed in July 2003). The EML building is approximately 55 m high, and the

SODAR measured winds in 5 m increments 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. (At the time of this writing, SODARs are a key component of the DHS/UDP implementation. Our early work in this field gave us a strong position in the UDP mesonet program.)

A tracer release experiment was planned originally for Spring, then Summer of 2004. However, negotiations with NYC and the emerging DHS study, Urban Dispersion Program (UDP), delayed the release. At this time, a release is scheduled for March 2005. The experiment will be a study of contaminant dispersion in the streets around Madison Square Garden and is called MSG-05. The experimental plan calls for turbulent instrumentation on rooftops and on locations at street level such as utility poles and building setbacks. A second LDRD has provided funds for a proof-of-concept exercise using the PFT tracers with six different compounds.

The circulation of winds over the city and in the street canyons is dependent on tropospheric wind direction and boundary layer stability, and thus is highly seasonal. Therefore, in order for a record to be of value in ongoing studies, it is essential that it be collected for a year. All instruments operated with astounding reliability, providing encouragement that a continuous mesonet is an achievable goal.

During FY2004 the DHS (finally) introduced their urban meteorology program. Jerry Allwine of PNNL has been established as the head of the program. The primary responsibility for design, deployment, and maintenance for the instrumentation mesonet and for instrumentation for the planned Intensive Operation Period (IOP) experiments, of which MSG-05 is one of four, was assigned to BNL. Thus a reasonable funding level is planned for the next three years at least.

SPECIFIC ACCOMPLISHMENTS:

Boundary Layer Winds Over New York City: A 15-Month Comparison of SODAR and Rooftop Anemometer, Reynolds & Smith is in preparation and pre-review.

LDRD FUNDING:

FY 2003	$70,000
FY 2004	$72,951

Application of Thin Film-Like Dosimeters for Port Security and Anti-Terrorism

Edward Kaplan *03-081*
J. Lemley
L. Milian
T. Tsang

PURPOSE:

To evaluate the feasibility of using commercially available, inexpensive, passive integrating neutron dosimeters for the purpose of *real-time remote detection* of radioactive materials concealed in cargo containers or onboard ship.

APPROACH:

A commercially available neutron-sensitive dosimeter based on superheated emulsion (SE) technology is widely used at research facilities. Thus far these devices, manufactured by a Canadian company [Bubble Technology Industries (BTI)], have found their predominant use for personal dosimetry. They provide qualitative information on the [fast] neutron flux encountered, and are usually read manually by counting the number of bubbles found in the emulsion, after which the device must be initialized before further use. The objective of this project was to develop an inexpensive capability to read the detector electronically, providing a semi-quantitative estimate of neutron exposure, and wirelessly transmit results on a real-time basis to a distant location using web-based technology.

TECHNICAL PROGRESS AND RESULTS:

During the first year of this project three types of dosimeters were evaluated by exposure to ^{252}Cf sources of different strengths. Two [thermoluminescent detectors (TLDs) and polycarbonate thin-films (PCs)] were tested and rejected because they required extensive processing before they could be evaluated. The third type of detector (known as a bubble detector) was based on superheated emulsion technology and was found to be capable of quickly responding to neutron exposure and being evaluated without further processing except visual inspection.

The objective of the second year of this project was to convert the visual response of the bubble detector into a digital signal via an inexpensive electronic readout that can be remotely interrogated, and that would periodically broadcast its status. The signal would then be fed into a commercially available asset tracking system [e.g., one that uses a self-configuring network to wirelessly connect to a remote transmitter using satellite technology to broadcast to a home base]. The signal that is broadcast would either be qualitative (e.g., more than some preset level) or quantitative (signal strength proportional to number of bubbles).

An early version of an electronic readout was developed with the assistance of Mr. Larry Milian (Environmental Research & Technology Division, Environmental Science Department) using light emitting diodes and photocells connected to a voltmeter. It was shown that the voltage output was proportional to the number of bubbles using bubble detectors exposed to ^{252}Cf sources for varying time periods. The principal investigators then enlisted the assistance of Mr. Thomas Tsang of BNL's Instrumentation Division, who developed a compact device (see Figure 1) that was extensively tested by exposure to ^{252}Cf

sources for time periods ranging from hours to many days. The experimental arrangement was remotely monitored by using a local access network (LAN) that transmitted data to PCs in the offices of Mr. Tsang as well as the principal investigators. Reproducible results (Figure 2) demonstrated the feasibility of remote, real-time interrogation of the otherwise passive neutron detector.

A nuclear detection web has been proposed that will utilize a digital readout for an advanced version of a bubble detector. In addition, the apparatus will be equipped with a unique electronic identity, GPS hardware, and wireless communication that will allow the radiation measurement, alarm status, identity, and location of the device to be transmitted to a network and its command center. This combination of detectors with a data management network creates a detection web whose first tier, interfacing detectors to a local network, will provide local authorities with continuous, automated monitoring of multiple detectors. At the second tier, data from these local networks will be aggregated and transmitted to a remotely located command center to provide another layer of functionality: federal departments and security agencies will receive radiation detection data from multiple locations (e.g. ports, transportation routes, critical infrastructure), leading to a threat assessment. BNL and BTI will partner with several Canadian agencies that will participate in field tests of the system (e.g., Canada Customs and Revenue Agency, Transport Canada, and Defence Research and Development Canada – Ottawa).

SPECIFIC ACCOMPLISHMENTS:

A patent was filed for both the apparatus and concept of real-time, worldwide, remote, web-based readout. Simple cellphone technology was used to demonstrate the wireless transmission of an optical readout signal from a bubble detector (Figure 3). Figure 4 shows actual test results in the form of a hypothetical application at various locations at BNL (as well as what a web-based data collection system might display on a remotely located PC).

BNL entered into a non-disclosure agreement with BTI and a joint proposal was developed for the Canadian Chemical, Biological, Radiological or Nuclear Research and Technology Initiative (CRTI). The proposal has been funded.

LDRD FUNDING:

FY 2003	$110,000
FY 2004	$100,696

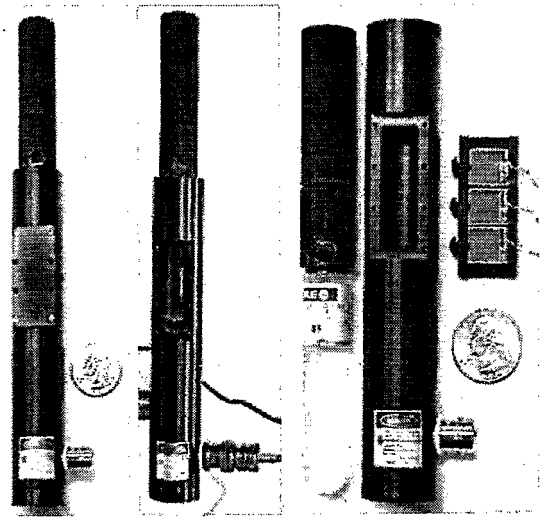


Figure 1 – Prototype Optical Readout Module for Neutron Detector

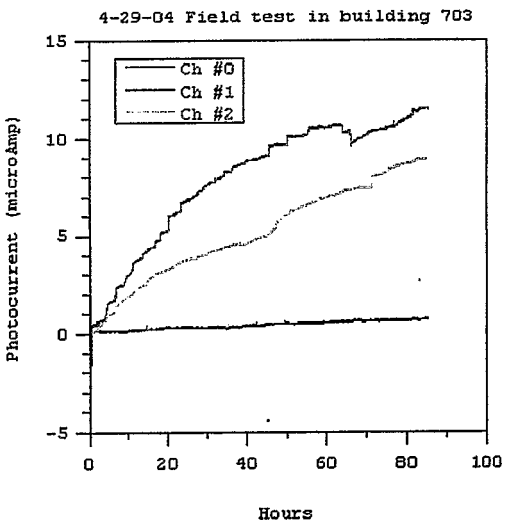
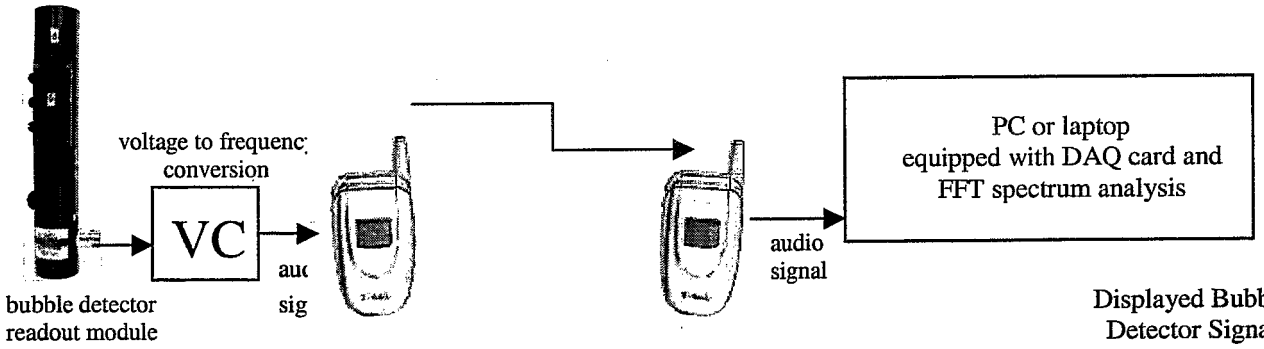


Figure 2 – Dose – Voltage Relationships – Four Day Bench-Top Exposures



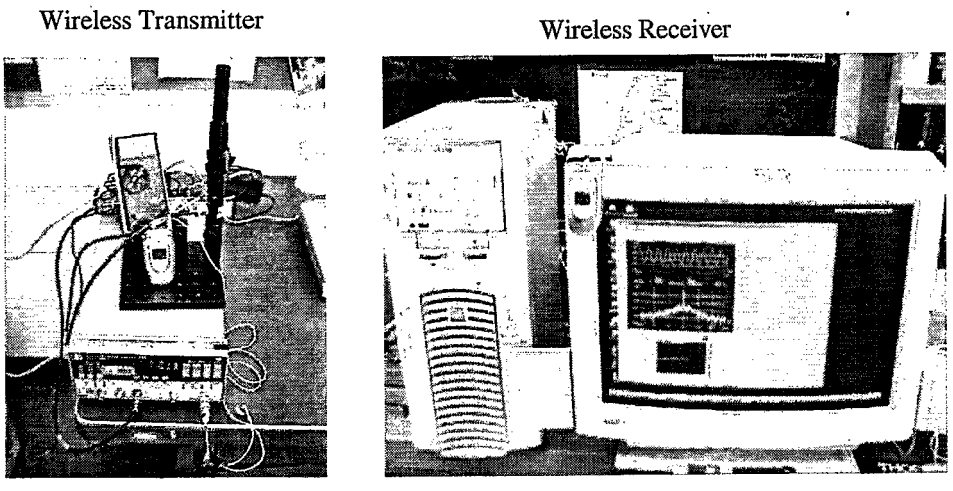


Figure 3 – Wireless Transmissions Setup

Neutron detection using bubble detectors – BNL field test

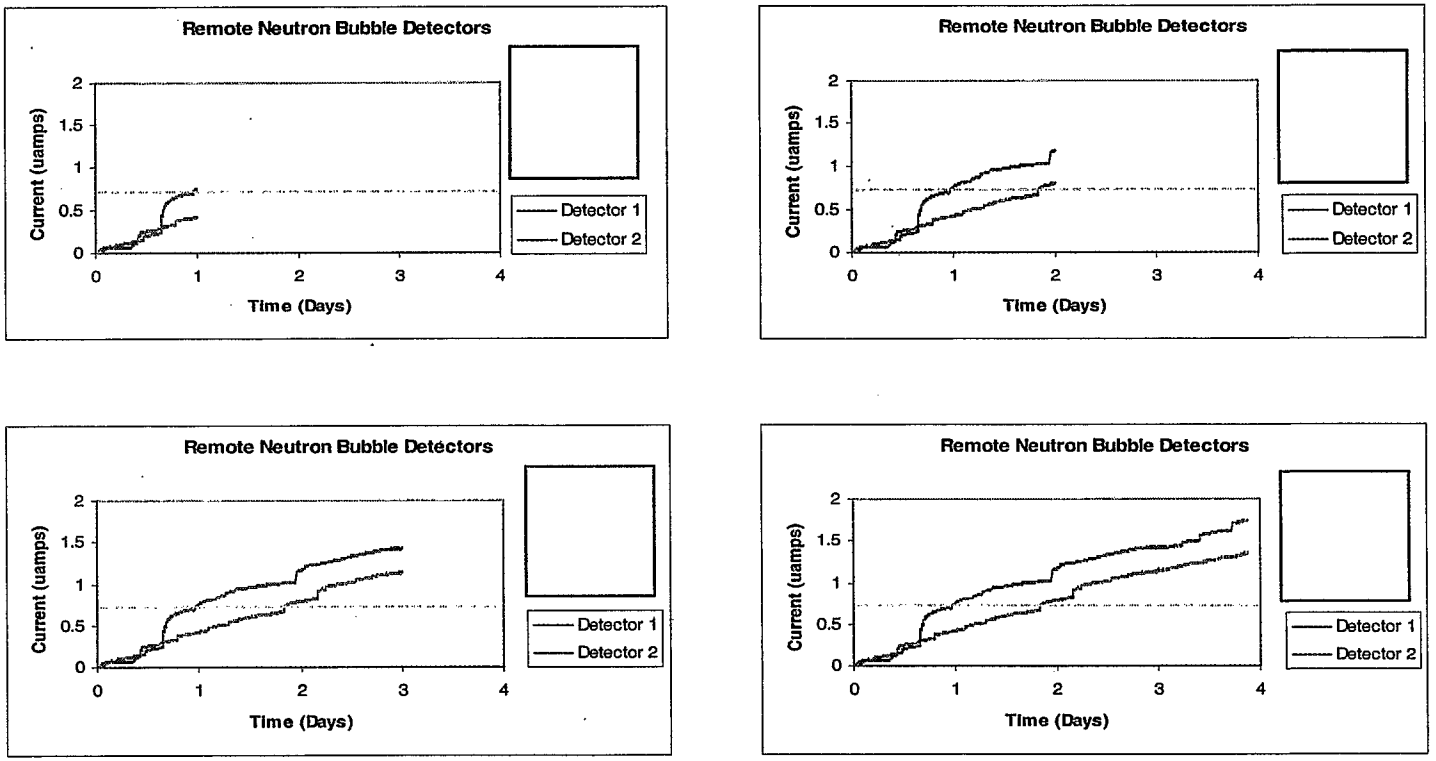


Figure 4 - Wireless Communication with Neutron Detectors

Novel Xenon Detector Concepts for Homeland Defense

Peter Vanier *03-083*
C. Salwen
G. Smith
D. Makowiecki

PURPOSE:

This project supported an effort to explore 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 was not optimized for a field-operable instrument. A detailed understanding of the factors limiting detector performance is needed in order to design and construct large volume prototypes for stand-off detection of special nuclear materials and radiological dispersal devices.

APPROACH:

The technology requires 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 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 aimed 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. The development of software for automatic isotope identification based on spectra from the xenon detector was a part of this effort. Other considerations that affect the applicability of the technology to specific tasks include portability, ease of operation, power consumption, and durability.

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. One new component chosen for very low power consumption was a novel chain of tera-ohm resistors for applying appropriate voltages to the field-shaping rings and the Frisch grid.

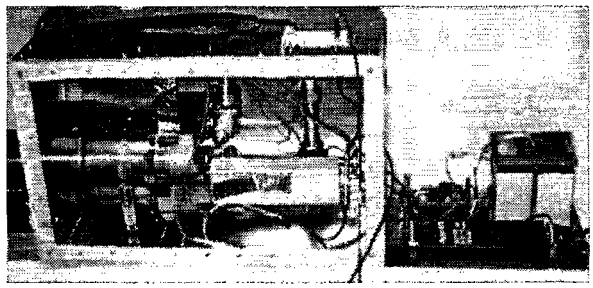


Figure 1. Xenon spectrometer with new electronics package.

The reconstructed system was tested with a series of check sources to demonstrate the spectral resolution and stability of the system. At first, there were problems with the new electronics. A number of sensitive preamplifiers were destroyed by transients in the charging cycle, and the spectral resolution was slightly inferior to earlier published results. This raised questions as to whether (a) the purity of the xenon in the chamber had degraded over a period of several years or (b) the new electronic system was noisier than the original one, possibly because of the tera-ohm resistor chain.

Eventually, after a painstaking series of trouble-shooting experiments, the main problem was eliminated by replacing the high-voltage relay with a more robust variety. Apparently, arcing inside this component had contributed to noise in the preamplifiers. The spectrometer now operates with very good resolution (2.5% at 662 keV) indicating that there has been no degradation in the purity of the xenon over a period of nearly 8 years.

Software was created for automatically analyzing the data and comparing unknown spectra to a library of common radioisotopes. The task involved selecting regions of interest, stripping peaks from the continuum, and performing a statistical comparison with stored templates. The method to distinguish targeted sources from medical isotopes or natural background is critically dependent on the spectral resolution and is more feasible for xenon than for low-resolution sodium iodide spectrometers.

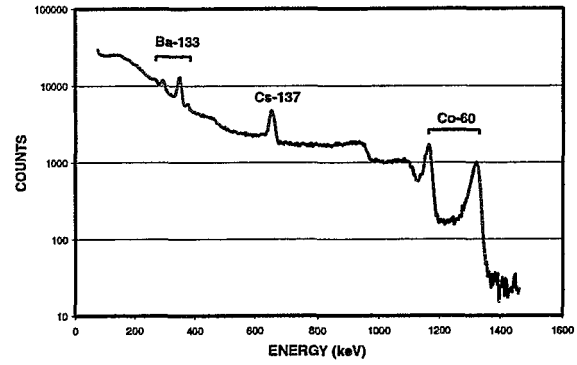


Figure 2. Spectra of Ba-133, Cs-137, and Co-60 showing isotopic identification capability.

SPECIFIC ACCOMPLISHMENTS:

New Hire:
Dr. Aleksey Bolotnikov, widely recognized as an expert developer of xenon spectrometers, is now the Principal Investigator of the DHS project on large-area xenon arrays.

Proposals submitted:
DHS: "High Pressure Xenon Detector Array," funded $400k ('04) and $350k ('05).

DOE/NA-42: "Hand-held Gamma-Ray Search Detector for Rapid Survey," $100k in FY04.

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$103,976

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 blocks 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 un-vaccinated 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 metallo-proteinase 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 a non-secreted form of LF in *E. coli*. In addition to the expected full-length LF protein, *E. coli* lysates also contained an approximately equal amount of a smaller fragment, which we determined was derived from the N-terminal region of LF. Furthermore, this N-terminal fragment was not observed in *E. coli* cells expressing LF mutants that have disrupted enzymatic activity. Together these observations suggested that LF digests itself to generate the N-terminal protein fragment.

As noted above, LF assembles with another component of anthrax toxin, the "protective antigen" (PA) protein, to form the holotoxin on the external surface of human cells. LF-PA complexes enter cells by endocytosis, and LF is then transported across the endosomal membrane through channels formed by hepatmeric rings of PA. Importantly, the mechanism by which LF dissociates from PA during its transport across the endosomal

membrane is not understood. Diphtheria toxin also consists of protease and carrier-protein subunits, which form hetero-oligomers on the cell surface, and the protease subunit dissociates from the carrier subunit by an autoproteolytic mechanism. Autodigestion of LF in the *E. coli* cytoplasm observed in our study suggested that LF dissociation from PA also may occur by an autoproteolytic mechanism. Autodigestion of LF further suggested that LF may have broad substrate specificity, cleaving more cellular proteins in addition to mitogen activated protein (MAP) kinase, which was identified as a substrate in an earlier study. Identification of all substrates digested by LF will be essential for full understanding of the intoxication mechanism, and for development of inhibitors and antidotes that interfere with substrate digestion by LF.

TECHNICAL PROGRESS AND RESULTS:

Our major objective this past year was to further characterize LF autoproteolysis by genetic and biochemical approaches. As noted above, the N-terminal fragment of LF resulting from autodigestion was not observed in *E. coli* cells that expressed LF mutants with amino acid changes in the protease active site. Contrary to expectation, however, there was no detectable increase in the amount of full-length LF protein in cells expressing inactive LF mutants. On closer examination, we observed that three extra protein species related to LF accumulated in *E. coli* cells that expressed inactive LF mutants. Further analysis showed that these extra species also were N-terminal fragments of LF, but they were greater in size (molecular weight) than the single major species observed in cells that expressed the active (wild-type) LF protein. Three different inactive LF mutants were analyzed, and the identical set of N-terminal fragments was observed in all three cases. The concentrations of the three truncated species in cell lysates, estimated from Western blot analysis, summed to approximately the same concentration as the single N-terminal fragment found in lysates of cells expressing the wild-type protein. Taken together, these observations suggested that the larger truncated species in mutant-expressing cells may be precursors to the smaller truncated protein that accumulates in cells expressing wild-type LF.

LF protein has a central region composed of five calcium-binding modules closely related to the calcium-binding EF-hand structure of calmodulin. The five modules have nearly identical amino acid sequences, and are encoded by five regions of nearly identical DNA sequence. These regions in the LF gene contain a high frequency of tandem rare codons, which have been shown to cause ribosome pausing or premature termination in other gene systems. Based on these analyses and other supporting data not described here, our current working model is that translation of LF mRNA terminates prematurely at a frequency of about 50%, generating full-length LF protein and several LF species truncated at different points in the calcium-binding region. In cells expressing wild-type, active LF, these truncated forms are trimmed back by LF proteolysis to generate a single truncated species, while in cells expressing inactive LF mutants the truncated species persist. This model supports the hypothesis that LF has broad substrate specificity, and consequently that many cellular proteins in addition to MAP kinase may be substrates for this enzyme.

SPECIFIC ACCOMPLISHMENTS:

We are currently preparing a manuscript to document the results of the autoproteolysis study.

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$ 99,543

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 expressed to high levels, 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 simplifyobtaining structural information for this particular integral membrane enzyme.

TECHNICAL PROGRESS AND RESULTS:

The postdoctoral research associate, Mary Lynn Baniecki, was hired in May of 2003 and left the project in November of 2003 to pursue a health-related postdoctoral project in Boston. There was a gap in staffing on this project until spring of 2004 when Ingo Heilmann started working on AlkB. He had little experience in this area and that was his motivation for wanting to work on AlkB, to gain experience in membrane protein expression and purification.

The amount of purification needed to produce samples consistent with structural analysis is reduced proportionately as the relative abundance of active protein in the membranes of the host organism increases.

We have been focusing on three factors, 1) bacterial host strain for expression, 2) media composition and 3) scale of induction. Media composition is important because commercial media component preparations are prepared in batch and have very complex sets of components. These components can vary between batches and we had experienced very different expression levels of AlkB at different times in the same bacterial host and same scale of expression. Results using different complex media components suggests that each AlkB construct should be under the control of a viral inducible promoter that should only be activated under conditions in which a specific chemical inducting agent has been added. However, in fact minor components, or combinations of media components can serve to cause the expression of the target protein at the wrong time in the growth cycle of the bacterial host. Such uncontrolled expression of the target protein has the effect of causing a lack of growth in the bacteria and hence a lack of yield of cells containing AlkB. Because expression at the correct

time results in high levels of protein expression, we conclude that the AlkB polypeptide itself is not the cause of toxicitiy, rather cessation of growth is likely the result of AlkB displacing other necessary proteins from the membranes. Thus, we explored various synthetic defined medias for the growth of AlkB. At the same time we needed to evaluate several different bacterial hosts that contain the DE3 lysogen (i.e., the T7 RNA polymerase under the control of a lac promoter). We chose to examine BL21, BL21 gold, BL21pLysS. Based on work from the labs of Studier and Fu, we initiated a new approach. Fu had been testing new bacterial growth media formulated by Studier in which the gene of interest under the control of the T7 RNA polymerase promoter becomes "autoinduced," meaning that the gene of interest is switched on in the absence of the classical inducing agent isopropyl thio-β- D-galactopyranoside (IPTG).

Summary of Progress

- Preparation of new strains of AlkB in a pET3a or pET9a plasmids in host cell lines BL21DE3, BL21DE3pLysS.
- Test growths of the above strains in TB media, rich ZYM 5052, defined + amino acids MA5052, and defined M5052 media.
- Demonstration that ZYM5052 gives better induction than MA5052 which gives better induction than M5052.
- Evaluation of different oxygenation conditions by growths of different quantities of media in different capacity vessels tubes versus flasks, baffled versus non-baffled flasks.
- Demonstration that growth of 1 liter of culture in a 2.8 liter baffled Fernbock flask can yield 2.7g of cells using the medium MA5052.
- Optimal protein was obtained from cultures inoculated with cells grown from a single colony in MGD media followed by storage at –70C and dilution into MA5052 media for growth of 1 liter cultures in baffled Fernbock flasks.

SPECIFIC ACCOMPLISHMENTS:

Shanklin, J. and Whittle, E. Evidence linking the *Pseudomonas oleovorans* alkane ω-hydroxylase, an integral membrane diiron enzyme, and the fatty acid desaturase family. FEBS Letters 545: 188-192 (2003).

LDRD FUNDING:

FY 2003	$55,000
FY 2004	$95,700
FY 2005 (budgeted)	$40,000

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 induced 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.

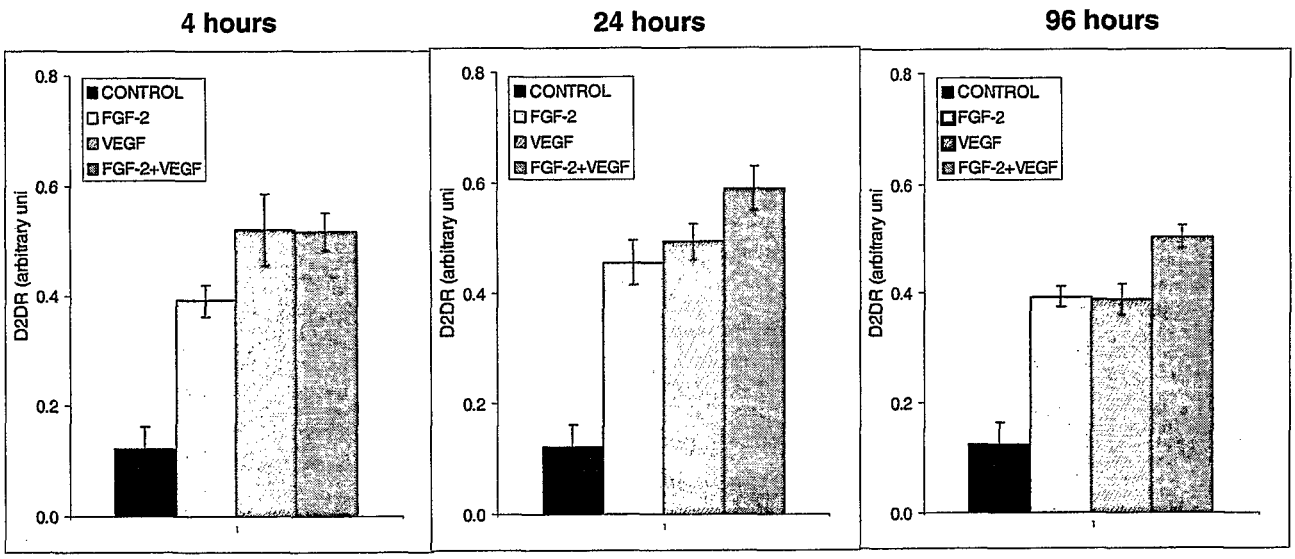
APPROACH:

Preclinical and clinical data suggest 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 Vascular Endothelial Growth Factor (VEGF). Dopamine, a catecholamine neuro-transmitter, recently has been the focus of 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. The inhibitory effects on angiogenesis leads one to hypothesize that dopamine receptors can be a target for antiangiogenic treatments and also a potential target for imaging tumors. To test these hypotheses, the expression of a dopamine receptor in endothelial cells treated by angiogenic inducers like FGF2 and VEGF was examined. Furthermore, using an in vitro angiogenesis model, the differential expression of dopamine receptor between endothelial cells that are in angiogenic stage and resting stage was studied.

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 that attracts future extramural funding from a variety of federal and private extramural funding agencies.

TECHNICAL PROGRESS AND RESULTS:

FGF2 and VEGF induced D2DR expression in BAECs:



The above figure shows that there is a FGF2 induced dopamine receptor on the D2DR protein expression in bovine aortic endothelial cells (BEACs). Another potent angiogenesis inducer, VEGF, also produces a similar effect on D2DR expression. The elevated D2DR expression appears as soon as 4 hours after FGF2 and VEGF treatment and lasts at least up to 4 days. This finding supports the hypothesis that there are dopamine receptors on the endothelial surface and their level will be elevated upon angiogenesis.

Dopamine receptor expression in endothelial cells involving in angiogenesis.

Using the in vitro angiogenesis model, we found that the elevated D2DR expression primarily takes place in the endothelial cells that are involved in angiogenesis (Figure below). This differential expression pattern of D2DR in angiogenic endothelial cells further proves the concept of using dopamine receptors as a specific target in the imaging of angiogenesis.

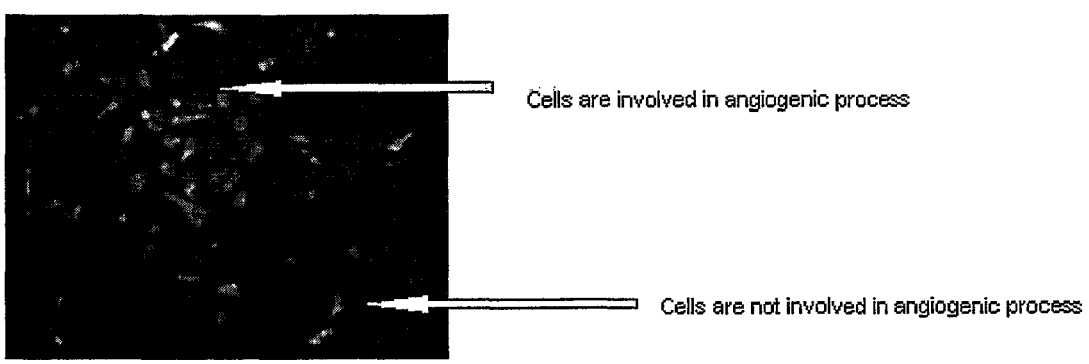
The findings from this year and in FY 03 will be the basis of a manuscript describing D2DR agonist as an anti-angiogenic agent, and there is a differential expression pattern of dopamine receptors in angiogenic endothelial cells. The differential expression pattern of dopamine receptors also proves the concept that dopamine receptors might be utilized as an imaging target for noninvasive imaging of cancer metastasis.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$ 99,091



The microPET Study of Gene Expression in Rodents

P. Thanos *03-099*

PURPOSE:

The chief objective of this research is to develop methods and assess the potential of micro Positron Emission Tomography (PET) 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 overexpress the gene in specific brain areas and in mice in which through knockout or knockin 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 has 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 "knockout" and "knockin" 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 knockout animals. Finally, methods employed include micro PET 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 knockout and (b) DAT wild type, DAT heterozygous and DAT knockout. 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. 4. Evaluated the sensitivity of microPET to assess functional brain changes as measured by regional brain glucose metabolism in: Transgenic DAT mice that were treated with a DAT blocking drug (cocaine).

For next fiscal year the following are planned:

Complete the evaluation of the sensitivity of microPET to assess functional brain changes as measured by regional brain glucose metabolism in rats with regional DAT who are treated with a DAT blocker drug.

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. (2004). DRD2 Gene Transfer into the Nucleus Accumbens of the Alcohol Preferring (P) and Non Preferring (NP) Rats Attenuates Alcohol Drinking. Alcohol Clin Exp Res. May;28(5):720-8.

~Ding, Y.S.; Gatley, S.J.; **Thanos, P.K.**; Shea, C.; Garza, V.; Xu, Y.; Carter, P.; King, P.; Warner, D.; Taintor, N.B.; Park, D.J.; Pyatt, B.; Fowler, J.S.; Volkow, N.D. (2004). Is the *l-threo* Enantiomer of MP (Ritalin) Inactive in the Brain when the Drug Is Given Orally? Synapse. 2004 Sep 1;53(3):168-75.

~Wang, G.J.; Volkow, N.D.; **Thanos, P.K.**; Fowler, J.S. Similarity between obesity and drug addiction as assessed by neurofunctional imaging: a concept review. J Addict Dis. 2004;23(3):39-53.

~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 ^{11}C-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 [^{11}C] raclopride and microPET. J Nucl Medicine. 43(11): 1570-1577. (2002).

~**Thanos, P.K.**, et al. 2004. Society for Neuroscience (SfN) Annual Meeting, San Diego, CA Oct 22-28. Presented **6** posters at this conference and 1 at last years SfN conference.

LDRD FUNDING:

FY 2003	$50,000
FY 2004	$94,700
FY 2005 (budgeted)	$50,000

Investigation of the "Early Response" in Functional MRI

Thomas Ernst *03-100*

PURPOSE:

Functional magnetic resonance imaging (fMRI) allows the non-invasive observation of brain activation. Although fMRI has had a significant 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 ultra-fast 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 project 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:

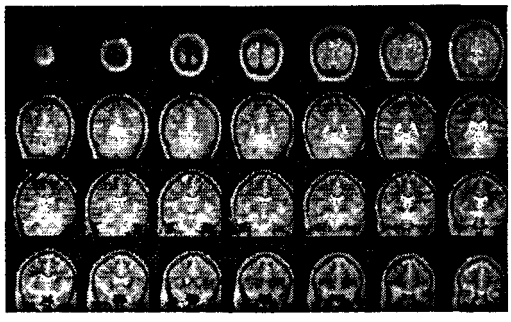
Phase I of the project required significant technical developments, which were completed in FY 03. First, a computer movie was created which shows a flickering checkerboard to stimulate the visual cortex. Given the transient nature of the "early response," software was written to precisely synchronize 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. In FY 04, efforts were focused on constructing a surface coil to further improve the signal to noise ration (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.

Thirteen human subjects were recruited into phase I of the project. Eight of these

subjects were scanned to optimize the scanner sequence (see above), and the remainder of the subjects were presented with the flicker board stimuli. The data from these preliminary studies were evaluated. The "early response" seems to be detectable in most of the subjects. The reliability and consistency of data from these experiments was not established, so phase II was not initiated to assess the physiological mechanisms underlying the "early response."

Substantial amounts of data were acquired to show the theoretical presence of the "early response" and its benefit to fMRI scans. The series of scans shown below used approximately 80% less RF power deposition and the acquisition time was reduced by a factor of 4-6.

This project involves human subjects.



SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2003:	$240,000
FY 2004:	$123,500

PET Imaging of Violent Behavior

Gene-Jack Wang *03-101*

PURPOSE:

Violence is one of the most pressing social problems in the US 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. We investigated the possibility of using Positron Emission Tomography (PET) technology to understand the role brain circuits play in non-aggressive and aggressive behavior.

APPROACH:

We hypothesize that high-trait aggressive individuals enjoy viewing violent images more so than do low-trait aggressive individuals and that their brain will show a different pattern of activity to the violent stimuli than low-trait aggressive individuals. In this project we assessed the effect of a violent (R-rated) video presentation as compared to a control video presentation, on glucose metabolism in healthy male subjects that were pre-classified as low or high-trait aggressive based on several aggression measurements.

TECHNICAL PROGRESS AND RESULTS:

*1) **Technical progress:*** Pre-classifying subjects from the general population as high and low-trait aggressive is the most difficult challenge in this project. This is due to the fact that most men are at neither ends of this extreme. We, therefore, had to reject most potential subjects in order to obtain only those who fall in either extreme (e.g., high-trait aggressive or low-trait aggressive). Ninety subjects were first screened by contact through telephone. Sixty of these subjects were again screened and interviewed at BNL to determine eligibility on the screening visit. The healthy subjects were selected and classified as "aggression prone subject" (AP) and "non-aggression prone subject" (NP) based on the overall evaluation of responses to Buss-Perry Hostility Inventory (BPHI), which consists of a questionnaire on media using habits and the responses to the brief screening video. To date, 20 subjects have met our criteria and were recruited. Ten of them were classified as AP and 10 as NP. PET and [^{18}F] Fluro-D-Glucose (FDG) was performed to measure brain metabolic responses after: viewing a R-rated video, and a viewing a control video, and at baseline (no video). The video presentations started at 10 min before the FDG injection and continued during the time of tracer uptake for a total of 40 min. The PET scans started at 35 minutes after the FDG injection. The metabolic images were analyzed using regions of interests and statistical parameter maps (SPM99) methods. We also measured behavioral responses during the PET study.

*2) **Preliminary results:*** Six AP and 7 NP completed the PET scans. The two groups were comparable with race and social-economic background. These healthy male subjects were between 22 - 34 (mean: AP: 24.9±3.9 and NP: 26.4±4.1) years old with 12 - 16 (AP: 14.9± 1.0 and NP: 15.4±2.0) years of education. These subjects spent similar amounts of time on weekdays and weekends watching television. During the studies, both groups of subjects did not report significant difference in their feelings toward the control and R videos. However, with regard to liking of the video stimuli, the AP reported that they liked the R video ($p < 0.003$) better than the control video when compared with the NP. AP also reported the quality of the

R video as better ($p < 0.01$) than the control video when compared with NP. With regard to dislike of the video stimuli, AP reported disliking the control more than the R video ($p < 0.02$), see Table 1 as compared with NP who reported no differences in dislike between the R and control videos.

	AP		NP	
	Cont	R	Cont	R
Quality	2.96	3.50*	3.40	3.40
Interest	2.55	4.00	3.40	3.40
Liking	2.95	4.00*	3.00	3.40
Disliking	2.31	1.00*	2.60	2.40

Table 1. Comparison between control (Cont) and R-rated (R) videos in AP and NP (rated from 1 to 5, 1 was lowest and 5 was highest). (* $p < 0.05$)

Statistical parametric mapping (SPM) analysis (Figure 1) showed both AP and NP increased metabolic response ($p < 0.01$) in left lateral orbitofrontal cortex (OFC) when watching control as compared to R video. However, only the NP had significantly more metabolic response ($p < 0.01$) in the anterior cingular gyrus (ACG: BA 32) and rectal gyrus (RG: BA 32) only when viewing the R video. AP did not have these activations in response to the R video.

3) Interpretation of the preliminary results: The activation of lateral OFC when viewing the control video as compared to the R video was common in both AP and NP showing a significant difference in this area between the two video stimulations. The activation in ACG and RG in NP but not in AP while viewing R video implicates the implementation of inhibitory control mechanisms by the NP subjects while AP did not implement these inhibitory control areas of the brain. AP, thus, lacked this emotional response. These preliminary results indicated the feasibility of using PET technology to identify brain circuits involved with aggressive behavior. Based on these encouraging results, we are recruiting more subjects to increase the statistical power in order to complete this study and report these findings.

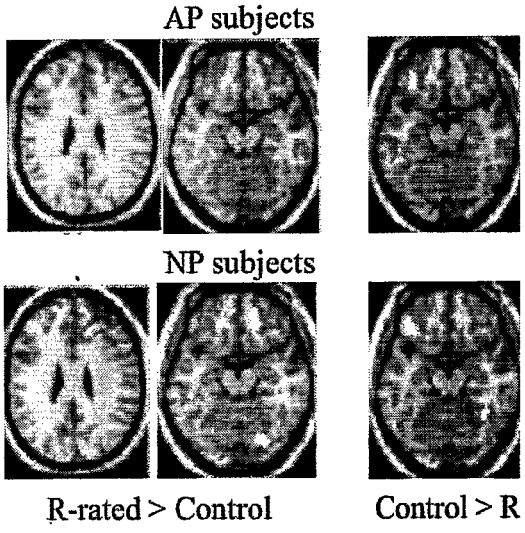


Figure 1. SPM results of metabolic response compared to viewing R-rated and control videos in AP and NP.

This project involves human subjects.

SPECIFIC ACCOMPLISHMENTS:

As a result of this project, two new fieldwork proposals were submitted to DOE and three grant proposals to NIH (NIH/NIDA, NARSAD and K award). The preliminary results from the subjects of this project evaluated with an fMRI paradigm targeting inhibitory control, was accepted as a slide presentation at the 2004 Annual meeting of the Society For Neuroscience entitled: "The word "no" activates areas associated with negative emotion and inhibitory control." In addition, the 'theme' of aggression/violence becomes the overall theme of DOE Center for Translational Neuroimaging roadmap: "How does the brain develop, mature and adapt to the environment."

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$ 98,978

PET Study Of Acetaldehyde Distribution And Metabolism To Better Understand Alcohol Related Diseases

Zizhong Li *03-103*

PURPOSE:

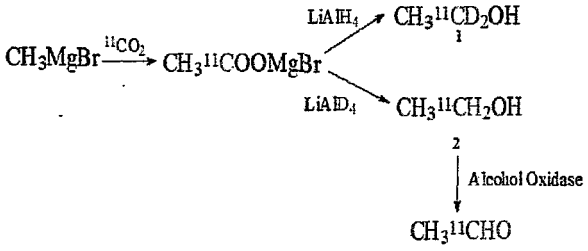
Although alcohol (ethanol) use is both well established and legally sanctioned, there is no illicit drug of abuse that has more devastating effects on the health of individual addicts or entails greater costs to society. Despite decades of research, there is much that remains mysterious about this scourge. The objectives of this LDRD project were to synthesize alcohol and particularly its toxic metabolite acetaldehyde with both carbon-11 and deuterium in suitable formulations for mechanistic Positron Emission Tomography (PET) studies.

APPROACH:

Our aim was to develop methods for radioactive synthesis, purification and formulation of C-11 ethanol and acetaldehyde and then conduct PET studies in monkeys. These would set the stage for human studies.

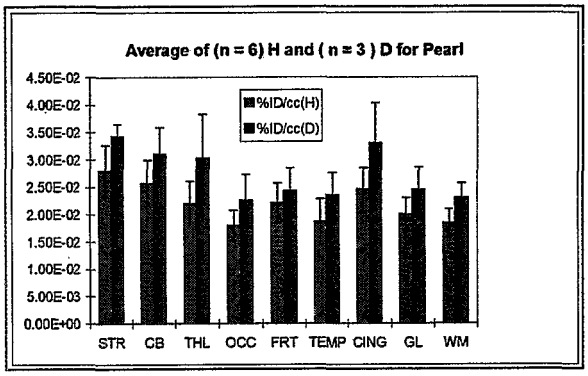
TECHNICAL PROGRESS AND RESULTS:

Radiotracer syntheses of C-11 labeled alcohol and deuterium labeled alcohol were developed and implemented without serious problems.

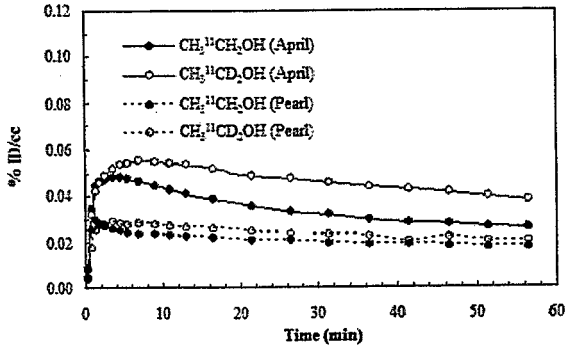


The main technical obstacles concerned maintaining chemical and radiochemical purities in a small volume of isotonic buffer suitable for intravenous injection ultimately (i.e. after obtaining appropriate grant support) into human subjects. High Performance Liquid Chromatography (HPLC) methodology was developed to achieve this goal.

PET imaging studies were conducted in babboons with the labeled alcohol. As anticipated, regional brain uptake of the deuterium substituted tracer appeared to be higher, a finding that we ascribed to reduced metabolism via the well known deuterium kinetic isotope effect on alcohol dehydrogenase. Brain regions examined were striatum, cerebellum, thalamus, occipital cortex, frontal cortex, temporal cortes, cingulate gyrus, global (ie whole brain) and white matter.

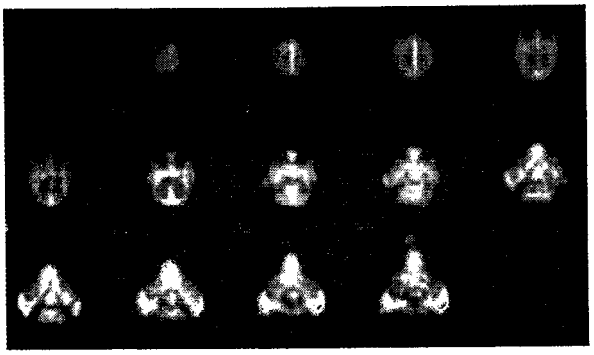


The kinetics of C-11 alcohol with and without deuterium substitution were measured in other organs. The figure below shows data for two different baboons (Pearl and April) in liver, the organ mainly responsible for metabolizing ethanol.

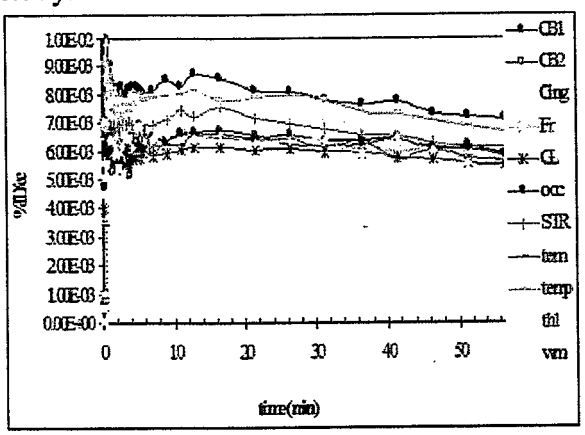


Both animals showed the expected longer residence time for the deuterium substituted tracer. Similar plots for lungs, heart and kidney showed little effect of deuterium substitution.

Following successful preparation of C-11 acetaldehyde, we have conducted the first PET studies with this compound



Uptake was low (perhaps one third to one quarter than of ethanol) but extracted tracer mostly remained in the brain throughout the study.



These 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 and acetaldehyde pharmacokinetics in normal controls and in alcoholic patients and to study other variables, such as gender, ethnicity (some groups are particularly sensitive to alcohol because they lack the enzyme that degrades acetaldehyde), and environmentally induced alcohol sensitivity.

We now plan to complete the PET studies of the C-11 labeled ethanol and acetaldehyde and publish results and apply for permission to do human studies, and use the results obtained from this LDRD research as preliminary data for an application to NIH grants to make funds available to continue this research.

This project involves animal vertebrate subjects and was approved by the Institutional Animal Care and Use Committee of Brookhaven National Laboratory, and the baboons were housed and maintained in an accredited animal husbandry facility that was approved by Association for Assessment Laboratory Animal Care.

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	$ 98,889

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 a new method for reaction of the carbon-hydrogen (C-H) bonds in hydrocarbons, 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.

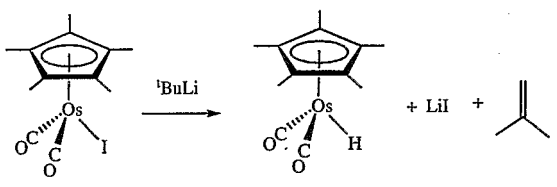
APPROACH:

A fundamental understanding of reaction mechanisms is required for the rational design of new homogeneous catalysts. Both kinetic and thermodynamic issues are important in assessing the viability of new proposed steps that might be used in catalytic cycles. Accordingly, we seek to gain an improved understanding of the reactivity of metal complexes that catalyze organic reactions. Selective conversion of hydrocarbons to functionalized organic compounds presents a formidable scientific and practical challenge, and is a major goal of organometallic chemistry and homogeneous catalysis. The most frequently used pathway for C-H bond activation is generation of a coordinatively unsaturated metal complex that reacts with hydrocarbons by an "oxidative addition" mechanism. We are examining an entirely different type of reaction, in which cleavage of a C-H bond proceeds by hydrogen atom transfer from the hydrocarbon to a metal-centered radical. Our initial studies focus on the use of osmium (Os), a metal that is known to form very strong bonds to hydrogen.

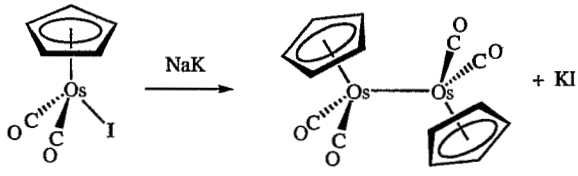
The osmium complexes that are being initially examined contain Os-Os bonds that can be cleaved photochemically to generate metal-centered radicals. We will seek to measure the rate constants for hydrogen atom transfer reactions. Experiments using transient infrared spectroscopy measurements will be carried out in collaboration, Dr. Etsuko Fujita and Dr. David Grills, both of whom have much experience in flash photolysis and transient infrared measurements.

TECHNICAL PROGRESS AND RESULTS:

A new postdoctoral research associate, Dr. Jie Zhang, arrived at BNL in April 2004. A notable problem that has previously 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 early efforts have sought to develop promising routes to complexes containing Os-Os bonds. The osmium iodide complex $Cp^*(CO)_2OsI$ ($Cp^* = \eta^5$-C_5Me_5) can be prepared in three steps from commercially available OsO_4. We have developed a high-yield route for conversion of $Cp^*(CO)_2OsI$ to the hydride complex $Cp^*(CO)_2OsH$, as shown below. This reaction provides $Cp(CO)_2OsH$ in 60% yield, and does not require elevated temperatures or high pressure equipment as in a previously

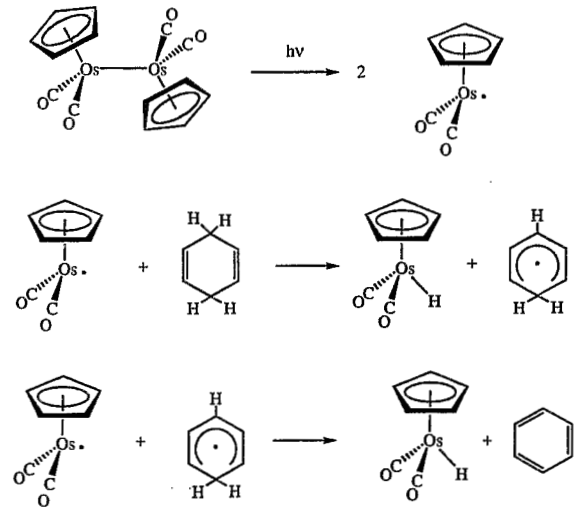


reported preparation. The Os-Os bonded dimeric complex $[Cp^*(CO)_2Os]_2$ ($Cp^* = \eta^5$-C_5Me_5) was previously reported in very low yield (4%). We have found that $Cp^*(CO)_2OsH$ can be converted to $[Cp^*(CO)_2Os]_2$ in 46% isolated yield through reaction with 2,2'-azobisisobutyronitrile. A different route was optimized for the synthesis of $[Cp(CO)_2Os]_2$ ($Cp = \eta^5$-C_5H_5). Reduction of $Cp(CO)_2OsI$ with NaK at room temperature led to the isolation of $[Cp(CO)_2Os]_2$ in 77-94% yield.



This is a substantial improvement in yield, and with fewer steps required, compared to literature reports. This reaction is thought to proceed by reduction of the osmium iodide to the osmium anion $[Cp(CO)_2Os]^-K^+$, followed by reaction of this anion with $Cp(CO)_2OsI$ to give the desired dimer. Long reaction times are detrimental since metal-metal bonded dimers can be subsequently reduced by NaK.

Initial experiments show that the intended carbon-to-metal transfer reaction does occur. Photolysis ($\lambda > 300$ nm) of a solution of $[Cp(CO)_2Os]_2$ and 1,4-cyclohexadiene produces two equivalents of $Cp(CO)_2OsH$, with benzene as the organic product. The proposed mechanism is shown below. Photochemical homolysis of the Os-Os bond produces osmium-centered radicals. Hydrogen atom transfer from the hydrocarbon to the metal-centered radical produces an organic radical that then donates a second hydrogen atom, producing the observed product, benzene.



Future research will seek to (a) measure the rate constants for these hydrogen atom transfer processes, (b) determine the detailed photochemistry of the Os-Os dimers to evaluate CO loss vs. metal-metal bond homolysis, (c) determine the bond dissociation energy of the Os-H bond in $Cp(CO)_2OsH$, (d) determine the structures by single crystal x-ray crystallography of one or both of the metal-metal bonded dimers, and (e) investigate the generality of the reaction by exploring a wide ranger of metals and potential hydrocarbon donors.

SPECIFIC ACCOMPLISHMENTS:

Bullock, R.M.; Dioumaev, V.K.; Kimmich, B.F.M.; Zhang, J. An invited talk, Ionic hydrogenations using proton and hydride transfer reactions of metal hydrides and hydrogen atom transfers of osmium complexes, will be given at a symposium at the 229th National American Chemical Society Meeting to be held in San Diego, CA, March 13-17, 2005.

LDRD FUNDING:

FY 2003	$20,000
FY 2004	$56,480
FY 2005 (budgeted)	$58,000

Radioprotection in D. radiodurans, a Radiation Resistant Bacterium

Diane Cabelli *03-105*

PURPOSE:

Deinococcus radiodurans is a bacterium that is extremely resistant to gamma radiation. Great interest in this organism led to its complete genomic sequencing in 1999. When the superoxide dismutase (SOD, metalloenzyme that dismutates superoxide (O_2^-) to O_2 and H_2O_2) is cloned out of the organism, the radiation resistance drops significantly. Understanding the mechanism of this bacterial superoxide dismutase (MnSOD) would help us to understand a large component of radioresistance exhibited by this organism and to address possibly engineering radioresistance into other organisms. 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 has, in some cases, been translated into reality. The involvement of this particular bacterium lies in its extreme radiation resistance. Efforts to engineer remediation function into D. radiodurans or to enhance the bacterium's existing ability to reduce heavy metals are underway elsewhere. Understanding the basic differences between D. radiodurans and other organisms with regards to MnSODs, membrane components and membrane surface may allow us to engineer radiation resistance into other bacterial systems that are already useful in non-radioactive cleanup.

APPROACH:

It has been proposed that Mn-SOD 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 the concentration of superoxide present.

$$Mn^{3+}SOD + O_2^- \xrightarrow{k1} Mn^{2+}SOD + O_2 \quad (1)$$

$$Mn^{2+}SOD + O_2^- \xrightarrow[+2H^+]{k2} Mn^{3+}SOD + H_2O_2 \quad (2)$$

$$Mn^{2+}SOD + O_2^- \xrightarrow{k3} Mn^{3+}SOD\text{-}O_2^{2-} \quad (3)$$

$$Mn^{3+}SOD\text{-}O_2^{2-} \xrightarrow[+2H^+]{k4} Mn^{3+}SOD + H_2O_2 \quad (4)$$

In order to understand an aspect of the extreme radioresistance of *Dr*, we studied the reactivity of its Mn-SOD with superoxide using the fast kinetic technique of pulse radiolysis found at BNL. This technique allows us to measure the rates of the individual reactions in the overall dismutation mechanism. We compared the reactivity of Dr MnSOD with that of e coli MnSOD and human MnSOD.

We then studied a mutant of MnSOD where the tyrosine in the second coordination sphere had been mutated to a phenylalanine. This mutation helps test what factors might control the gating between outer-sphere and inner-sphere reduction of superoxide.

Finally, we performed Density Functional Theory (DFT) calculations aimed at providing a detailed understanding of the energetics of each step, the transition state structures and the differences between the various enzymes and mutants.

Collaborators are:

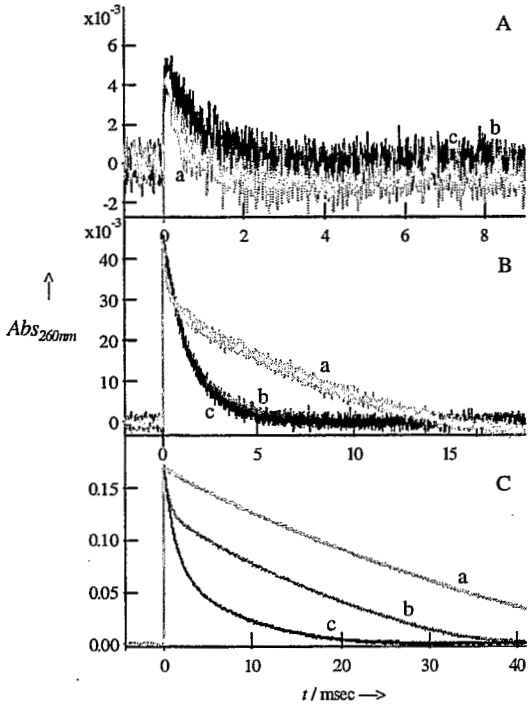
Professor David Silverman, University of Florida, for the expression, isolation, and purification of MnSOD from D. radiodurans.

Professor Geoff Jameson, University of New Zealand, for determination of the crystal structure of the MnSOD.

Dr. Jose Rodriguez, BNL, for the DFT calculations.

TECHNICAL PROGRESS AND RESULTS:

These results show that when compared to both the *E. coli* and human enzymes, the *Dr* Mn-SOD is able to deal with higher superoxide concentrations.



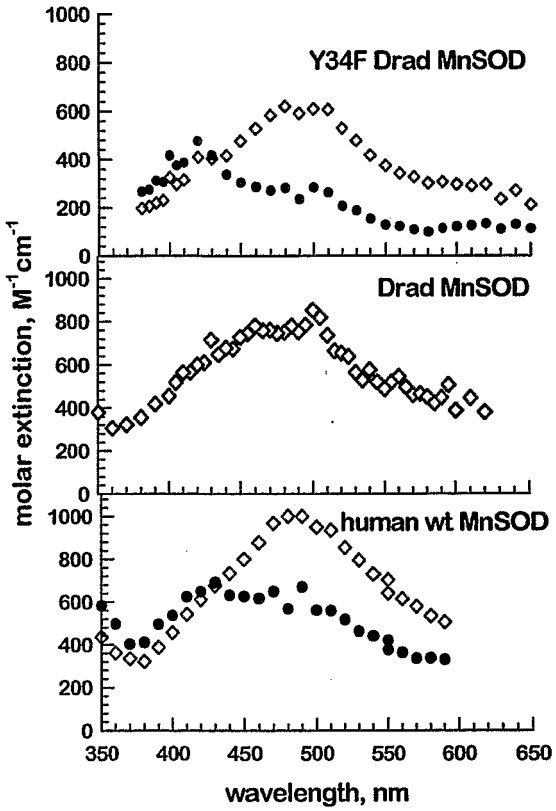
The traces show the disappearance of various concentrations of superoxide in the presence of varying amounts of MnSOD. In panel A, the superoxide and MnSOD are there in identical concentrations (5μM). Here, O_2^- disappears at equally fast rates for all of the enzymes; hMnSOD, e coli MnSOD and DrMnSOD. In equamolar concentrations, only k_1 or k_2 are accessed and the rate constants are identical.

Under catalytic conditions, however, where the ratio of O_2^- to MnSOD is 7:1 (panel B), the human enzyme is already noticeably less efficient at removing superoxide In the hMnSOD, the O_2^- is partitioning equally between the inner sphere and outer sphere mechanism and release of the bound peroxide becomes rate limiting.

In the presence of 43μM superoxide and 1 μM MnSOD (Panel C), the *E. coli* enzyme is now also partitioning between an inner sphere and outer sphere mechanism. The dramatic difference observed here is that within 3 milliseconds, over half the superoxide has disappeared in the presence of DrMnSOD, while less than 25% has disappeared in the presence of e coli MnSOD, and only a few percent has disappeared in the presence of human MnSOD.

This so far uniquely efficient dismutation ability 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. It has been shown that *Dr* Mn-SOD plays a role in radioresistance, since *Dr* cells lacking the enzyme are more susceptible to radiation

The three panels below show the spectra generated when a substoichiometric amount of superoxide is generated in the presence of an excess of Mn(II)SOD. Clearly, the Drad Mn(II)SOD is rapidly converted to Mn(III)SOD, consistent with the ratio of reactions 2:3 of 15. In contrast, the human Mn(II)SOD is converted to a 50:50 ratio of Mn(III)SOD (absorption maximum at 480 nm) and the transient MnSOD-superoxide adduct (absorption maximum at 420 nm). Interestingly, the Drad Y34FMn(II)SOD now reacts in a manner identical to the human MnSOD, with a 50:50 gating of k_2 and k_3. The role of the tyrosine 34 in this system needs to be further addressed both experimentally and theoretically.



SPECIFIC ACCOMPLISHMENTS:

I.A. Abreu and D.E. Cabelli, "The Kinetic Mechanism of Manganese-Containing Superoxide Dismutase from *Deinococcus radiodurans*: A Specialized Enzyme for the Elimination of High Superoxide concentrations," *in preparation.*

Isabel A. Abreu, José A. Rodriguez, and Diane E. Cabelli, "Bonding of O_2^- to Manganese and Iron Superoxide Dismutases: Role of the Second-Sphere of Coordination around the Metal Centers," J Phys Chem, *submitted.*

LDRD FUNDING:

FY 2003	$57,500
FY 2004	$74,668
FY 2005 (budgeted)	$17,500

New Development of Norepinephrine Transporter Radioligands for PET Studies of Substance Abuse, Depression and ADHD

Yu-Shin Ding *03-107*

PURPOSE:

Research on dopamine transporter (DAT) and serotonin transporter (SERT) 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 lack of suitable radioligands. The fact that all three transporters (NET, DAT and SERT) are involved in various neurological and psychiatric diseases places a sense of urgency on the development of 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-ethoxy-phenoxy) -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 positron emitter labeled analogues of reboxetine for Positron Emission Tomography (PET) imaging studies of NET in non-human primates. Dr. Kuo-Shyan Lin, an organic chemist in my lab, has synthesized numerous NET radioligands.

TECHNICAL PROGRESS AND RESULTS:

During FY2002, we identified the first promising lead compound, (S,S)-[^{11}C]MRB, which displayed in vivo specificity and selectivity for PET imaging of NET. Building on this exciting new development, and on our strengths in tracer development, translational studies and substance abuse research, we proposed to develop and evaluate a series of new NET tracers in FY 2003. We also carried out studies to quantify NET occupancy and the duration of action by the stimulant drugs cocaine (Coc) and methylphenidate (MP).

Although space-constraints prevent a detailed description of our studies, these results demonstrate our experience and expertise in this area, and the promising data obtained from the evaluation of [^{11}C]MRB support the success of this approach.

1. Synthesis and evaluation of (R)-[O-$^{11}CH_3$]- and (R)-[N-$^{11}CH_3$]Nis

2. Synthesis and evaluation of a C-11 labeled reboxetine analogue ([^{11}C]MRB)

3. Synthesis and evaluation of F-18 labeled reboxetine analogues ([18F]FRB)

4. Measurement of lipophilicity (log P) and plasma protein binding (PPB)

5. Occupancy of NET by Coc and MP

These preliminary studies demonstrate:
(1) We are able to synthesize several novel NET radioligands, including (R)-[O-$^{11}CH_3$]Nis, (R)-[N-$^{11}CH_3$]Nis, C-11 and F-18 labeled reboxetine analogues and their individual (R,R) and (S,S) enantiomers

([^{11}C]MRB, [^{18}F]FRB-H_4 and [^{18}F]FRB-D_4). The novel strategies for the preparation of precursors, radiotracers and chiral separation provide methods for future development of new, structurally related radioligands. To our knowledge, (S,S)-[^{11}C]MRB is by far the most promising in vivo NET radiotracer for PET imaging studies in the brain; with adequate selectivity, pharmacokinetic and metabolism;
(2) F-18 labeled reboxetine ([^{18}F]FRB-D_4) has fast kinetics and may also have potential as a suitable PET ligand;
(3) The promising results from the initial studies in baboon to measure the NET occupancy by Coc and MP support further investigation of the role of NET in the action of psychostimulants in human subjects.

We continued to make significant progress and also accomplished the following studies:

6. Synthesis of [^{11}C]reboxetine ([^{11}C]RB)

7. Synthesis and evaluation of 3-Cl-[^{11}C]MRB

8. Synthesis and evaluation of [^{11}C]oxaprotiline

9. Synthesis and evaluation of [^{11}C]lortalamine

10. Asymmetric synthesis to obtain single enantiomer (S,S)-[^{11}C]MRB

11. Evaluation of tracer metabolism

12. Transgenic mice study

13. Co-registration with Magnetic Resonance Imaging (MRI)

14. Improved Kinetic Analysis (a new modeling approach to the identification of a reference region) and its application to occupancy studies.

Our additional studies demonstrate the following:
(1) We continue to successfully develop new NET radioligands, including [^{11}C]RB, (S,S) and (R,R) enantiomers of [^{11}C]3-Cl-MRB, [^{11}C]oxaprotiline and [^{11}C]lortalamine;
(2) Tracer evaluation in baboons indicated: (a) (S,S)-[^{11}C]3-Cl-MRB displayed desired properties that are similar to our lead compound, (S,S)-[^{11}C]MRB; (b) although high brain uptake is desirable, the high non-specific uptake in ST and low signal to noise ratio lead us to conclude that [^{11}C]oxaprotiline is not a suitable ligand for in vivo NET imaging studies; (c) [^{11}C]lortalamine is better than [^{11}C]oxaprotiline; however, it still suffers high non-specific uptake in ST;
(3) We are able to carry out asymmetric synthesis to prepare a single, enantiomerically pure, precursor that can be used directly for the radiosynthesis of (S,S)-[^{11}C]MRB;
(4) Our tracer metabolism study in mice demonstrated that radiolabeled metabolites do not enter the brain and are not likely to contribute to the PET images;
(5) Studies in NET knockout mice and wild type controls further support results from our previous baboon studies, demonstrating that (S,S)-[^{11}C]MRB is a selective ligand for brain NET;
(6) PET-MRI co-registration in baboons has improved the reliability of ROI placement;
(7) Our improved kinetic analysis method using DVR (distribution volume ratio) calculated by using an average of OCC (occipital cortex) and BG (basal ganglia) as the reference region has provided more reliable quantification in our occupancy studies.

Taken together, the knowledge and expertise we gained from our preliminary studies will

guide us to design the studies that we will carry out further for preclinical investigation, and also set the stage for further investigation of the role of NET in the action of psychostimulants in human subjects.

Summary

To our knowledge, (S,S)-[^{11}C]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)-[^{11}C]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 MicroPET studies using transgenic animals, particularly monoamine knockouts. Because of the importance of the monoamine neurotransmitters and their association with motor activity, cognition and mood, this will be an important advance.

Future Plan

In the coming year (2005), 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. Continue the occupancy studies of NET by Coc and MP.

3. Obtain funding from NIH.

4. Obtain approvals from the FDA and our IRB to carry out studies in human. This will require a toxicology study of the drug. GlaxoSmithKline (GSK) has agreed to fund this toxicology study, and is currently conducting the toxicity experiments.

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:

1. Presentation of our results at the DOE Review meeting in Boston, 27-29 Oct., 2003.

*Ding, Y.-S.; Lin, K.-S. Synthesis and evaluation of new norepinephrine transporter PET ligands in non-human primates. A poster presentation.

2. Publication of two peer-reviewed articles:

*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* 16:475-481 (2004).

3. Presentation of our findings to several international scientific symposia:

*Ding, Y.-S. and Lin, K.S. Development of new norepinephrine transporter PET ligands in non-human primates. Presented to *DGN (Society for German*

Nuclear Medicine), Frankfurt, Germany, April 21-25, 2004.

*Ding, Y.-S.; Lin, K.S.; Logan, J.; Fowler, J.S.; Volkow, N.D. Occupancy of brain norepinephrine transporters by cocaine and methylphenidate. Presented to the *51st Annual Meeting of the Society of Nuclear Medicine*, Philadelphia, PA. June 19-23, 2004. *J Nucl Med* (Suppl) 45:69p.

*Ding, Y.-S.; Lin, K.S. PET imaging studies of norepinephrine transporters. Presented to the 34th Annual Meeting of the Society for Neuroscience, San Diego, October 23-27, 2004.

*Biegon, A.; Caron, M.; Cyr, M.; Fowler, J.S.; Lin, K.S.; and Ding, Y.-S. [^{11}C]S,S-methylreboxetine; a new PET ligand for norepinephrine transporters (NET): autoradiographic evaluation in NET knockout mice. Presented to the 34th Annual Meeting of the Society for Neuroscience, San Diego, October 23-27, 2004.

*Lin, K.S. and Ding, Y.-S. A facile one-pot approach to the preparation of aryl [^{11}C]ethyl ethers from [^{11}C]iodomethane: synthesis of C-11 labeled reboxetine. Presented to *51st Annual Meeting of the Society of Nuclear Medicine*, Philadelphia, PA. June 19-23, 2004. *J Nucl Med* (Suppl) 45:438p.

*Lin, K.S.; Kim, S.; and Ding, Y.-S. Synthesis and evaluation of F-18 labeled reboxetine analogs as PET tracers for norepinephrine transporter. Presented to the *51st Annual Meeting of the Society of Nuclear Medicine*, Philadelphia, PA. June 19-23, 2004. *J Nucl Med* (Suppl) 45:106p.

We have submitted an NIH grant application in March, 2004. Although a non-fundable score was obtained, the review was extremely encouraging. We therefore submitted a revised application in November 2004. We hope and believe that we will be able 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.

LDRD FUNDING:

FY 2003	$112,000
FY 2004	$111,095
FY 2005 (budgeted)	$ 93,000

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 ground-breaking work in the short-wavelength regime in chemical physics, photo-dissociation, 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, on photoelectron imaging, on pump-probe photodissociation dynamics, on surface dynamics and on non-linear ionization of rare gases, where the simultaneous absorption of two or more photons liberates a bound electron.

APPROACH:

Brookhaven 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 manner, the DUV-FEL at the Source Development Laboratory (SDL) 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 an 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 relying 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 Basic Energy Sciences (BES) Fundamental Interactions program.

TECHNICAL PROGRESS AND RESULTS:

Funding for this effort began October 1, 2002, and the endstation, shown in Fig. 1, was assembled and detected the first XUV photons from the DUV-FEL in December, 2002.

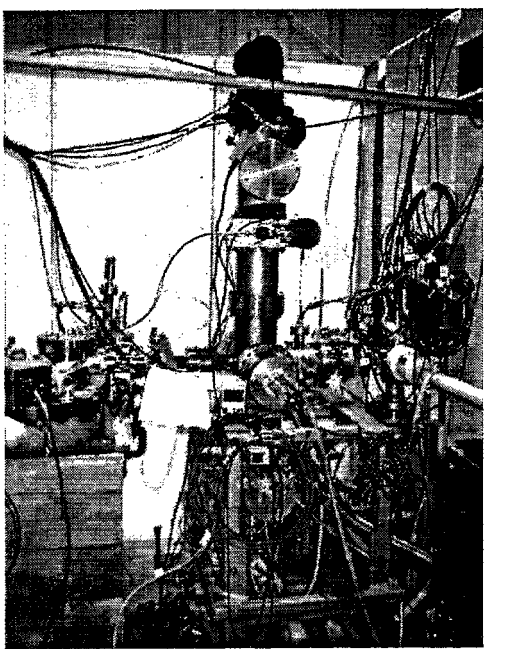


Figure 1. Imaging endstation at the DUV-FEL

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.

Milestones achieved 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 in collaboration with the Houston group at Cornell University.

SPECIFIC ACCOMPLISHMENTS:

Results were published in *Physical Review Letters 2004,* and the paper was selected for the online journal *Virtual Journal of Ultrafast Science.* "Superexcited state dynamics probed with an extreme-ultraviolet free electron laser," Li, W.; Lucchese, R.; Doyuran, A.; Wu, Z.; Loos, H.; Hall, G.E.; and Suit, A.G.

This work was presented in posters at a symposium on "VUV probes of spectroscopy and dynamics" at the 225th national ACS meeting in March, 2003, and at the Waterloo Chemical Physics symposium in November, 2003.

In addition, it was featured in numerous invited lectures presented throughout the world. It was included in 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.

Efforts to develop a joint proposal between Chemistry and the SDL to be submitted to DOE were extensively considered but have recently been abandoned following discussions with DOE.

LDRD FUNDING:

FY 2003	$132,000
FY 2004	$131,367

Imaging Tandem Mass Spectrometry for High-Throughput "Fingerprint" Detection of Complex Molecules in Mixtures

Arthur G. Suits *03-115*
G. E. Hall

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, NIH, 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 the 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 will couple velocity map imaging with tandem mass spectrometry to achieve an imaging tandem mass spectrometry (iMS^n). This promises to yield 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:

The apparatus was fully assembled and commissioned in FY04.

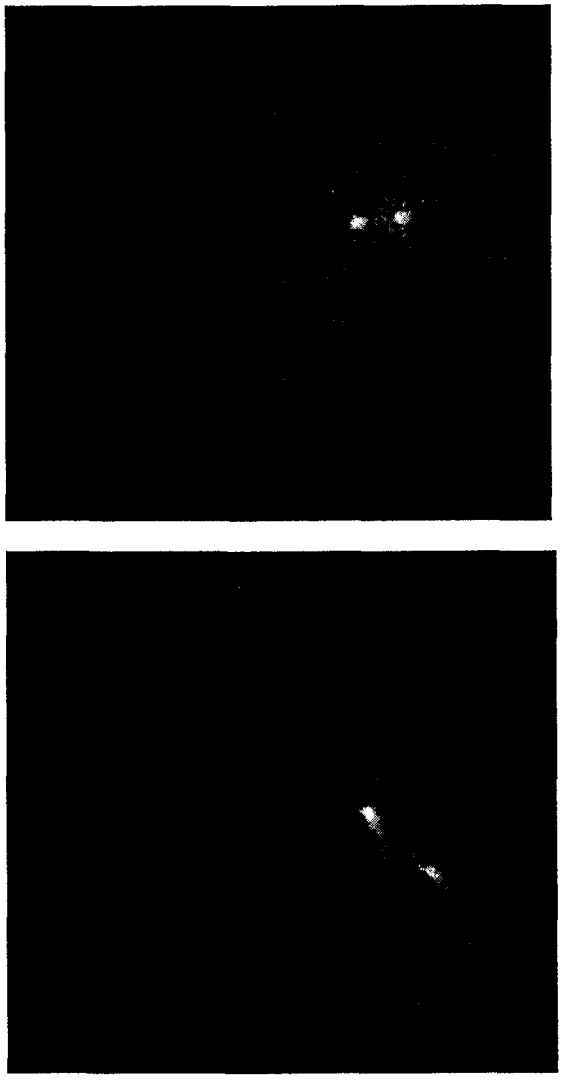


Figure 1. Spatially-resolved mass dispersion demonstrated (upper); tandem mass spectrometry demonstrated (lower).

The milestones achieved by the project in the final year 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 (see Figure 1).

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2003	$113,000
FY 2004	$109,593

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 Laser-Electron Accelerator Facility (LEAF) facility is uniquely suited to this work. Results of this study may lead to new, ionic liquid-based initiatives in photochemical energy storage, including (H_2 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 has been 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 Profs. Robert Engel and Sharon Lall-Ramnarine of City University of New York (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, with Prof. Mark Kobrak of Brooklyn College, CUNY on molecular dynamics simulations of solvation phenomena, and with Prof. Steven Greenbaum of Hunter College, CUNY, on nuclear magnetic resonance (NMR) studies of transport phenomena in ionic liquids.

"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.

TECHNICAL PROGRESS AND RESULTS:

Pre-solvated electrons in ionic liquids and their solvation processes were directly observed for the first time, using the new near-infrared (NIR) pulse-probe capability at LEAF. Last year's LDRD-funded development of low-viscosity, fully saturated ionic liquids made the work possible. We have found that electron solvation occurs hundreds or thousands of times slower in some ionic

liquids than in molecular solvents. We can now compare electron solvation dynamics with the laser-induced solvation time obtained from the fluorescence Stokes shift of coumarin 153 in the same solvent (see below). Detailed pulse-probe electron solvation studies are underway.

In collaboration with Ed Castner, variable-temperature time-domain fluorescence Stokes shift and polarization anisotropy decay measurements were obtained and analyzed in detail for five ionic liquids. The results show that solvation times to scale with viscosity, and range from 100 ps to 200 ns (viscosity 10 – 10,000 cP).

The radiation chemistry of carborane-based ionic liquids and of carborane salts dissolved in other ionic liquids was studied. The main absorbance transient was identified as an oxidation product of the $CB_{11}H_6Br_6^-$ anion. Electrons were observed to quickly react with $CB_{11}H_6Br_6^-$, likely followed by dissociation of Br^-.

A new generation of "criticality-safe" ionic liquids containing our low-viscosity cations and neutron scavenging *bis*(oxalato)borate (BOB) anions were synthesized by this year's Faculty and Student Team. We are eager to study their radiation chemistry because of potential applications in the nuclear fuel cycle. Our earlier work indicates that CO_2 is very soluble in ionic liquids and an excellent pre- and solvated electron scavenger. We wish to explore the possibility of using a CO_2/CO_2^- /oxalate cycle to reduce cumulative radiation damage in ionic liquids, just as in nuclear reactors where H_2 is added to avoid net water radiolysis.

Studies of the electron solvation process in ionic liquids using NIR pulse-probe will be expanded during the final year of the project. Attempts will be made to directly measure pre-solvated electron scavenging rates by pulse-probe. Pre-solvated electron reactivity is a much more significant aspect of the radiation chemistry of ionic liquids than it is for ordinary solvents. Yields, spectroscopy and reactivity of primary species will be determined for additional classes of ionic liquids, particularly those containing BOB anions. Self-diffusion rates of ionic liquid components and solutes will be measured with an NMR 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:

One publication from this project has been accepted for the ACS Synposium Series volume resulting from the ionic liquids symposium at the 2003 New York ACS meeting, and another has been submitted to the volume for the 2004 Electrochemical Society (ECS) Molten Salts Symposium.

A ten PI, five year proposal for an NSF/DOE supported Environmental Molecular Science Institute was not funded but nevertheless resulted in the formation of the New York Regional Alliance for Ionic Liquid Studies (NYRAILS), a group of local academic and BNL investigators with broad-ranging research interests who collaborate on ionic liquid research and respond to funding opportunities. A subgroup of NYRAILS including this PI submitted an NSF Research Experience for Undergraduates proposal (pending) to establish a summer research program in ionic liquids, with the help of the BNL Office of Educational Programs. Four of us have recently submitted a Collaborative Research in Chemistry (CRC) preproposal to NSF on the dynamical properties of ionic liquids, combining experimental and theoretical approaches.

Invited talks on this work were given at the Philadelphia ACS Meeting, the Honolulu ECS Meeting, and the Radiation Chemistry Gordon Conference, and a nanoscience meeting in Osaka, as well as the October 2003 BNL

Lecture. Seminars were presented at Caltech, UCLA, UCSB, UCSD, UCR, CSLB, and CUNY Brooklyn.

An informational workshop on ionic liquids was held at BNL in April 2004. Three undergraduate summer research interns and one summer visiting professor were sponsored through educational programs to participate in this project. A similar number of participants will be working with us again next summer.

This LDRD project supports collaborations with researchers at several CUNY campuses, and it has helped to strengthen the relationship between BNL and the CUNY Alliance for Minority Participation.

LDRD FUNDING:

FY 2003	$43,000
FY 2004	$79,517
FY 2005 (budgeted)	$37,000

Exploring the Use of Powder Diffraction for Proteins

Marc Allaire *03-119*

PURPOSE:

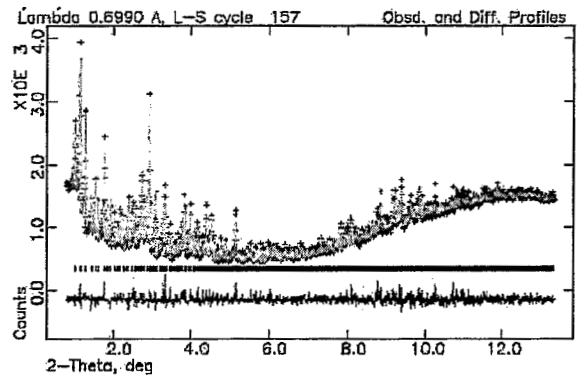
The discovery of ligands that would bind specifically to targeted proteins could have a dramatic impact in Life Sciences. We could infer, from the chemical nature of these ligands, possible biochemical activity and assign function to proteins. These ligands could also be used as probe, e.g. to observe phenotype in cellular assay, and identify cellular activity and function of these proteins. Moreover these ligands could be exploited in the process of drug discovery. The purpose of this proposal is to develop an X-ray based method such as Protein Powder Diffraction (PPD) to identify protein/ligand complexes.

APPROACH:

The goal of our approach is to use PPD to identify protein/ligand complexes from High-Throughput Screening (HTS) of a large library of chemicals. The approach is based on the idea that PPD data of bound and unbound proteins should be different. Recent work done by R. Von Dreele on lysozyme suggests the potential of PPD to locate ligands and infer the possibility of using PPD and HTS to describe the binding modes of a protein target. In our study we want to develop a simple method based on PPD data to identify protein/ligand complexes.

TECHNICAL PROGRESS AND RESULTS:

Our initial effort has shown that powder diffraction data could be acquired from lysozyme samples prepared by the addition of 2.0M of NaCl to 200mg/ml of protein in a mixing ratio of 1:1. This data has been subjected to restrained-Rietveld refinement and converged with a final χ^2 of 3.85 and good stereochemistry. The results of refinement for the observed and difference profiles are shown here.



We then tested the hypothesis that changes in PPD data should be observed in the presence of bound ligand. We used for this study N-acteylglucosamine (NAG) and $(NAG)_3$ which are known to bind lysozyme, and as negative controls a blank buffer and glucose. The chemicals were added in equi-molar concentrations to the lysozyme prior to the addition of NaCl. Powder diffraction data were collected for two ranges of 2θ (4-5°, 13-14°) for three samples of lysozyme, two samples mixed with glucose, two samples mixed with NAG, and three samples mixed with $(NAG)_3$. Pearson correlation coefficients between diffraction data were calculated and are presented here for 2θ of 4-5° (d-Bragg spacing ~9Å).

1.00	0.96	0.93	0.95	0.96	0.84	0.83	0.40	0.36	0.40
	1.00	0.97	0.98	0.95	0.86	0.85	0.44	0.39	0.44
		1.00	0.97	0.93	0.85	0.85	0.44	0.40	0.44
			1.00	0.95	0.84	0.84	0.42	0.37	0.42
				1.00	0.83	0.82	0.40	0.37	0.40
					1.00	0.98	0.47	0.43	0.46
						1.00	0.49	0.45	0.49
							1.00	0.94	0.94
								1.00	0.91
									1.00

+Glucose

+NAG

+$(NAG)_3$

These results indicate that correlation coefficients range from 0.91-0.98 for identical samples. It should be pointed out that the data were collected alternatively through all the different samples in order to avoid any correlation over time. The correlation coefficients obtained between data of free lysozyme and lysozyme mixed with glucose (0.93-0.98) compare well with identical samples and suggests that the addition of glucose does not affect the diffraction data. Similar comparison with NAG (0.83-0.86) and $(NAG)_3$ (0.36-0.44) suggest that these compounds cause a change in the diffraction profile. The results are also consistent in comparing glucose, NAG and $(NAG)_3$. These results indicate that we can group together similar samples and agree well with the expected ligand binding properties of these chemicals to lysozyme.

The correlation coefficients obtained at 2θ of 13-14° (d ~ 3 Å) are shown here.

1.00	0.93	0.93	0.92	0.91	0.90	0.88	0.86	0.81	0.82
	1.00	0.93	0.93	0.91	0.90	0.88	0.87	0.81	0.83
		1.00	0.93	0.92	0.90	0.88	0.87	0.81	0.83
+Glucose			1.00	0.91	0.90	0.88	0.87	0.82	0.83
				1.00	0.89	0.87	0.87	0.81	0.82
	+NAG				1.00	0.95	0.88	0.84	0.85
						1.00	0.87	0.82	0.83
							1.00	0.92	0.93
			+$(NAG)_3$					1.00	0.94
									1.00

Analysis of these data reveal a similar pattern, even though not so prominent, as for the data at a d-Bragg spacing of ~9 Å. The correlation coefficients obtained in comparing identical samples (0.91-0.95) or glucose and lysozyme (0.91-0.93) differ slightly from the ones in comparing NAG and lysozyme (0.88-0.90) or $(NAG)_3$ and lysozyme (0.81-0.87). These patterns are also consistent in comparing glucose, NAG and $(NAG)_3$ and suggest that we can group similar samples from PPD data. More importantly these results indicate that the signal obtained from powder diffraction data at a d-Bragg spacing of ~3Å is indeed sample-dependant.

The results presented above indicate that PPD could be used to identify protein/ligand complexes for lysozyme. Additional effort is now required to apply this technique for HTS application of protein of interest. Two main aspects need further development. Effort in the development of instrumentation is required to process multiple samples for HTS. The goal is to assess about one sample per second. Preliminary results suggest that this could be achievable. Further effort is also needed in the assay development of the protein of interest. So far PPD data of refineable quality have been obtained from lysozyme and thaumatin. PPD have also been observed from xylanase and β-lactamase, and in this process a new crystal form for xylanase has been found. Further funding support is now required in order to pursue this project in a competitive manner and to take advantage of X-ray based method for HTS in Life Sciences.

SPECIFIC ACCOMPLISHMENTS:

"A Simple Method for the Idneitification of Protein/Ligand Complexes Using Protein Powder Diffraction," (2004) presented at the following: The 8th International Conference on Biology and Synchrotron Radiation, Himeji, Hyogo, Japan; The Gordon Research Conference: Diffraction Method in Structural Biology, Lewiston, ME; and at the 2004 Annual Meeting of the American Crystallographic Association, Chicago, IL.

LDRD FUNDING:

FY 2003	$45,000
FY 2004	$79,445

Element-Resolved Dynamics of Nanoscale Ferromagnets

Chi-Chang Kao *03-121*
Darío A. Arena

PURPOSE:

The dynamical properties of engineered magnetic materials such as ultra-thin (<100 nm) films and other nanostructures are increasing in importance and relevance 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), or time-resolved magneto-optical Kerr effect (tr-MOKE) 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. The initial experiments under this LDRD have investigated the damping of precessional rotation of the magnetization in thin film samples of permalloy ($Fe_{20}Ni_{80}$). However, the techniques and expertise developed for the project can be applied to measurements of other magnetic systems, and further experiments are currently underway.

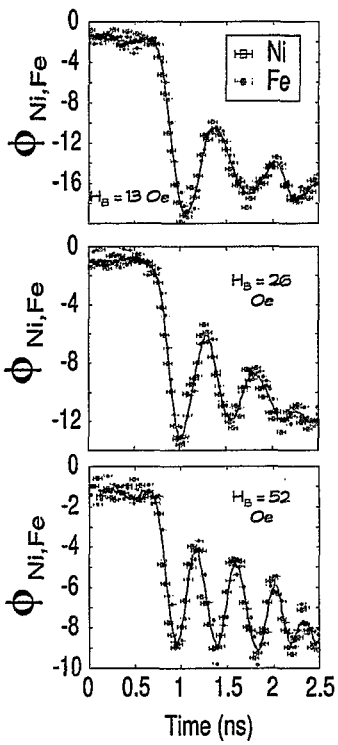
APPROACH:

X-ray magnetic circular dichroism (XMCD) is a standard synchrotron-based spectro-scopic technique for examining the magnetization of thin-film samples with element specificity. To achieve time-resolved XMCD measurements, we 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 (width ~100 um) in the waveguide. The microwave pulse initiates a rotation of the magnetization of the thin film about an axis perpendicular to the applied field. The magnetization of the sample then precesses around the applied field with an amplitude whose decay is described by a phenomenological damping constant. The microscopic origins of the damping constant has been a matter of controversy for over four decades. The damping constant can be modified with the addition of small amounts of rare-earth metals, such as Tb, into the alloy film. Standard FMR, tr-MOKE and similar techniques, however, can not address directly the role of the rare earth impurity in modifying the damping constant. With time-resolved XMCD, we can separately follow the magnetization of the Fe, Ni and Tb in the film and thus investigate the origin of the damping constant.

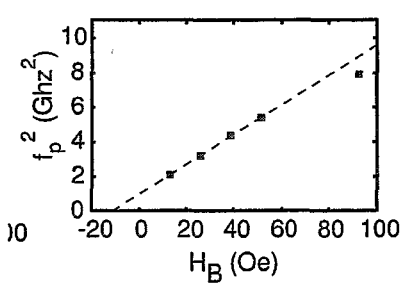
We carried out our initial experiments at the APS at Argonne National Laboratory. The APS offered a few advantages that are not readily available at the NSLS. Most importantly, the photon bunch length at the APS was quite short (~35 – 50 ps) and this greatly simplified the experimental architecture. By using such short pulses as a sort of element-specific and magnetization sensitive strobe light, we were able to set up a relatively simple pump-probe experiment where we synchronized a high-repetition rate, fast rise time pulser with the photon bunches at the APS, and then followed the magnetization dynamics by varying a delay between the magnetization pulse and the photon probe.

TECHNICAL PROGRESS AND RESULTS:

The initial experimental run was quite successful and we were able to separately follow the precession of the Ni and the Fe moments in a thin film of $Fe_{20}Ni_{80}$. The data, shown below, demonstrate, for the first time, the magnetization precession of elemental moments:



The custom-designed experimental chamber was equipped with Helmholtz coils oriented vertically, which allowed us to conduct a crucial test of magnetization precession: the linear increase of the precession frequency squared (f_p^2) with the applied bias field from the Helmholtz coils:



The initial experimental run at the APS demonstrated the feasibility of time-resolved XMCD and its application to investigating long-standing gaps in our knowledge of ultrafast magnetization dynamics. Since then, we have improved the experimental apparatus considerably and are actively planning the next sets of experiments which will occur in December 2004.

In addition to these activities, we are exploring the use of advanced, ultrafast photon detectors to conduct these experiments at the NSLS. 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, a 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.

SPECIFIC ACCOMPLISHMENTS:

We successfully developed time-resolved XMCD with significantly improved time-resolution and applied this technique to a model system: an ultrathin film of $Fe_{20}Ni_{80}$. The results of this initial measurement will appear as: "Precessional dynamics of elemental moments in a ferromagnetic alloy," W.E. Bailey, L. Cheng, D. J. Keavney, C.-C. Kao, E. Vescovo, and D.A. Arena, Phys. Rev. B, *in press.*

LDRD FUNDING:

FY 2003	$30,000
FY 2004	$79,558
FY 2005 (budgeted)	$50,000

Membrane Biophysics Using Model Membranes

Ronald Pindak 03-122
L. Yang

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. In the previous fiscal year, we used x-ray scattering to study substrate-supported and free-standing lipid film under controlled environmental conditions (temperature and relative humidity), which lead to a variety of temperature- and hydration-dependent lipid structures and lipid-peptide complexes. In FY04, we started to study substrate supported single bilayers, which resemble biological membranes the most, but also is the most difficult to prepare and characterize among the three-model systems. These bilayers, with embedded membrane structures such as membrane proteins in the form of either 2-dimensional fluids or 2-dimensional crystals, will be studied by x-ray scattering using the synchrotron beam at NSLS. Since the bilayers are not stable in air and must be maintained under an aqueous buffer solution at all times, the characterization of these samples is non-trivial. The focus of our research in FY04 was to design and test sample cells that are suitable for x-ray scattering measurements. We also utilized Fluorescence Microscopy (FM) for monitoring the formation of the bilayers on the substrate and thus help optimize the sample preparation method.

TECHNICAL PROGRESS AND RESULTS:

In FY03, we studied bulk lipid structures that are relevant to the study of membrane fusion. We continued to work on lipid structure in substrate-supported films and discovered a lipid phase in which a modulated structure with square symmetry form within each one of the stacked lipid bilayers (Fig.1). This square phase structure belongs to a class of more general modulated structures, and some theorists

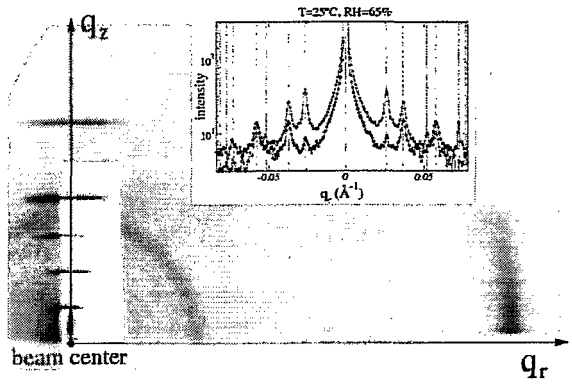


Figure 1. The diffraction pattern from the square phase of DTPC (13:0 hydrocarbon chains). Satellite peaks appeared around each layering peak (on the q_z axis) and clearly indicates the formation an in-plane lattice. The inset shows that the indexing of the satellite peaks agrees with a square lattice. The diffused peak at high q_r and centered at q_z=0 suggests that both the positional and the orientational order of lipid chain packing in this phase are distinct from and intermediate between those in the liquid crystalline phase and the gel phase.

have predicted its existence. Our scattering data showed that the periodicity of the square lattice is highly temperature and hydration dependent, and that the lipid chain packing in the square phase is distinct from that in the structures with flat bilayers. Studying the chain packing in the square phase and other modulated structures like the well-known ripple phase therefore may be the key to understanding the formation of these structures.

In parallel to the experiments with bulk structures, we have successfully prepared substrate supported single bilayers using liquid cells of two different designs (Fig.2). The first cell (Fig.2B, left) is very thin (~300μm) and has a window on either side of the cell that is transparent to both visible light and x-rays, which allows for both FM and transmission x-ray scattering measurements. For FM measurements, we utilize NBD-labeled lipids and Texas-Red-labeled Strepavidin to visually inspect the formation of the bilayer and the subsequent protein adsorption. The second cell (Fig.2C, inset) is used for X-ray reflectivity (XR) measurements and has an x-ray path length of 10mm. From the XR data, we were able to determine that the lipid layer adsorbed on the silicon substrate was ~40Å thick.

With the continued funding for this project in FY05, we plan to study lipid chain packing in the modulated phases and the organization of membrane proteins embedded in single bilayers.

SPECIFIC ACCOMPLISHMENTS:

L. Yang, L. Ding, and H.W. Huang, "New Phases of Phospholipids and Implications to the Membrane Fusion Problem," NSLS Science Highlights, Nov. 2003

L. Yang and M. Fukuto, "A Modulated Phase of Phospholipids with Two-Dimensional Square Lattice," submitted to Phys. Rev. Lett.

LDRD FUNDING:

FY 2003	$30,000
FY 2004	$79,316
FY 2005 (budgeted)	$50,000

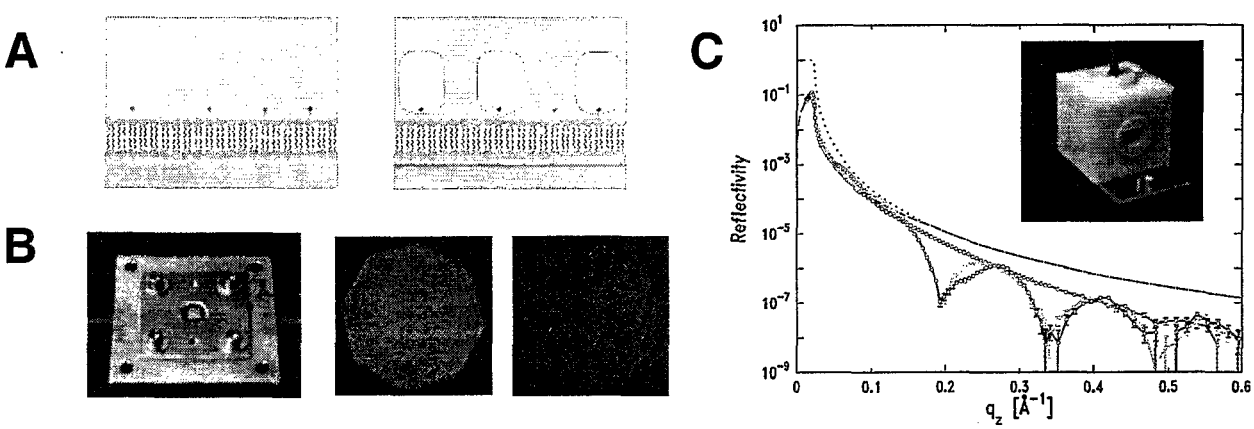


Figure 2. Two liquid cells were used to prepare supported single lipid bilayer (schematically shown in A, left) and a subsequent adsorbed protein layer (B, right). The first cell (B, left) has two windows that are transparent to both visible light and x-rays, which allows for both FM (micrographs in B, the green color is due to the NBD labels on the lipid molecules and the red color due to Texas Red labeled streptavidin) and transmission x-ray scattering measurements. The second cell (C, inset) is used for XR measurements. The XR curves in C are from the lipid bilayer (green), protein-adsorbed bilayer (red), and a bare silicon substrate (blue).

High Pressure in Strongly Correlated Materials – An Optical Investigation

Christopher C. 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 project has a high degree of technical difficulty. However, if successful this may constitute the basis for a new fieldwork proposal in the optical properties of materials under high pressure.

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 synchrotron provides an extremely bright source; through the use of optics that condenses 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.

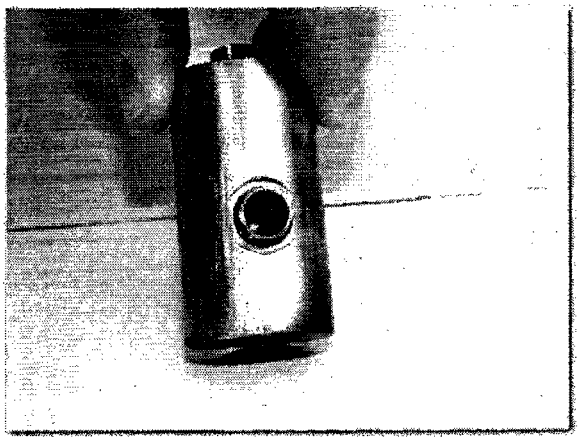
The high-pressure studies performed by the Materials Synthesis Group (T. Vogt) allowed us to exploit an existing knowledge base, rather than begin from scratch. Our interest has also shifted to a clamped pressure cell through a collaboration with the University of Budapest (G. Mihaly), which allows larger samples, in particular single crystals, to be examined.

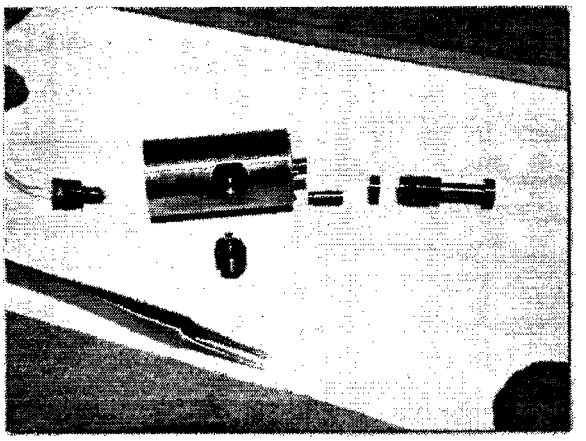
TECHNICAL PROGRESS AND RESULTS:

This project was first funded in the beginning of FY 2003. Initial actions were the hiring of a postdoctoral fellow, Dr. Sasa Dordevic, who arrived in December. A DAC suitable for optical studies was purchased, and a vacuum optical bench was constructed using off-axis parabolic mirrors (outlined in the first status report).

In FY 2004 the transmission bench was fully commissioned and initial studies of the effects of pressure on the high-dielectric constant material $CaCu_3Ti_4O_{12}$ were performed using quartz as a pressure calibration (quartz is preferable to ruby as it avoids having to use powerful class 3b lasers to determine the pressure in the cell). The transmission cell is well suited for insulating materials that are mainly transparent in the infrared region. However, it does not work well with metallic systems that are opaque. To this end, we have collaborated with Prof. G. Mihaly's group (Budapest, Hungary), to construct a clamped pressure cell with a large wedged diamond window. While this

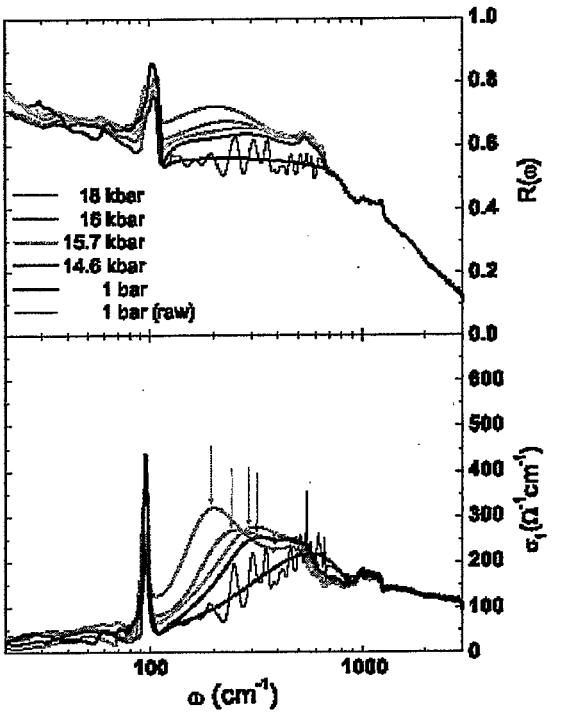
cell has a lower ultimate pressure (~25 kbar) than is achievable in a DAC (~80 kbar), it has a large sample volume that allows single crystals to be examined, rather than powders (shown in the figures below).





The cell is compact and threads into the bottom of a flow cryostat, allowing the effects of both temperature and pressure to be examined. Work will continue on improving the performance of the clamped pressure cell and the reflectance optics used with this cell.

An important result has been the measurement of the complex optical properties of the strongly-correlated material $BaVS_3$, which has a metal-insulator transition below ~ 70 K.



The conductivity (shown above, lower panel) at ~ 60 K indicates that the charge-transfer band shifts to zero frequency above a critical pressure ~20 kbar, resulting in the recovery of the metallic state.

SPECIFIC ACCOMPLISHMENTS:

Refereed publications:

"Energy scales in the high-T_c superconductor $YBa_2Cu_3O_{6+x}$," C.C. Homes, S.V. Dordevic, D. A. Bonn, Ruixing Liang and W.N. Hardy, J. Superconductivity **17**, 93-96, (2004).

"Sum rules and energy scales in the high temperature superconductor $YBa_2Cu_3O_{6+x}$," C.C. Homes, S.V. Dordevic, D.A. Bonn, Ruixing Liang and W.H. Hardy, Phys. Rev. B **69**, 024514 (2004).

"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, Phys. Rev. B. **69**, 094511 (2004).

"A universal scaling relation in high-temperature superconductors," C.C. Homes, S.V. Dordevic, M. Strongin, D.A. Bonn, Ruixing Liang, W.N. Hardy, Seiki Komiya, Yoichi Ando, G. Yu, N. Kaneko, X. Zhao, M. Greven, D.N. Basov, and T. Timusk, Nature **430**, 539-541 (2004).

"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. (cond-mat/0311335)

"Coherence and incoherence along the c axis of $YBa_2Cu_3O_{6+x}$," C.C. Homes, S.V. Dordevic, D.A. Bonn, R. Liang, and W.N. Hardy, submitted to Phys. Rev. B (cond-mat/0312211).

"Are high-temperature superconductors in the dirty limit?" C.C. Homes, S.V. Dordevic, T. Valla and M. Strongin, submitted to Phys. Rev. B (cond-mat/0410719).

"Extracting the electron-boson spectral function $\alpha^2F(\omega)$ from infrared and photoemission data using inverse theory," S.V. Dordevic, C.C. Homes, J.J. Tu, M. Strongin, T. Valla, P.D. Johnson, G. Gu, and D.N. Basov, submitted to Phys. Rev. B (cond-mat/0411043).

Conferences:

"Signatures of charge inhomogeneities in IR spectra of high-Tc cuprates," S.V. Dordevic (invited talk), March Meeting of the American Physical Society, Montreal, P.Q., Canada, March 22-26, 2004.

"A new method of extracting electron-boson spectral function $\alpha^2F(\omega)$ from infrared and ARPES spectra using inverse theory," S.V. Dordevic, C.C. Homes, J.J. Tu, T. Valla, M. Strongin, P.D. Johnson, G.D. Gu, and D.N. Basov, Bull. Am. Phys. Soc. **49**, 818 (2004). March Meeting of the American Physical Society, Montreal, PQ, Canada, March 22-26 (2004).

"Infrared optical properties of $HgBa_2CuO_{4+\delta}$," C.C. Homes, S.V. Dordevic, G. Yu, X. Zhao, and M. Greven, Bull. Am. Phys. Soc. **49**, 818 (2004). March Meeting of the American Physical Society, Montreal, PQ, Canada, March 22-26 (2004).

"A new method of extracting electron-boson spectral function $\alpha^2F(\omega)$ from infrared and ARPES spectra using inverse theory," S.V. Dordevic, C.C. Homes, J.J. Tu, T. Valla, M. Strongin, P.D. Johnson, G.D. Gu, and D.N. Basov, International conference on the Low Energy Electrodynamics of Solids, Kloster Banz, July 18-23 (2004).

LDRD FUNDING:

FY 2003	$54,400
FY 2004	$66,865
FY 2005 (budgeted)	$11,000

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. We are trying to explore an important fundamental scientific problem: "*When the size of single inorganic molecules reaching the orders of nanometers, what new sciences can we expect*?" We are particularly focusing on the unique solution properties of the giant POM anions. This project succinctly states in one short paragraph the technical objective or goal and the exploratory nature of the work pursued in the context of the current state of its technical field. This proposal fits in well with BNL efforts on nanoscience and condensed matter physics.

APPROACH:

Since the last decade, inorganic chemists have continuously synthesized giant POM molecules, pushing the size of inorganic compounds to the nanometer scale (The largest one was discovered at BNL). However, their physical properties have not been systematically studied. In the fields of nanoscience, the giant POMs offer "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.

Our 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, poly-electrolytes (e.g., proteins and DNAs) and hydrophilic colloids.

Laser and small-angle X-ray scattering techniques (X21C, NSLS), TEM (H. Li, Biology, BNL) and AFM (Y. Cai, Physics, BNL) are used for the study. Some samples were provided by Prof. Achim Müller at U. of Bielefeld, the leading synthetic chemist in the field of POM.

TECHNICAL PROGRESS AND RESULTS:

Significant progress has been made during the last two fiscal years. Although highly soluble and fully hydrophilic, POM and POM-based macorions still tend to self-associate into unknown supramolecular structures, which obviously contradicts our common understanding on soluble ions. We successfully determined that such strange structures actually had a unique single-layer vesicle structure and named it "blackberry." This discovery leads to the identification of a new type of self-assembly in nature and finally solves the historical "blue water" puzzle. A new universal solute state has been identified, resulting in the opening of a new field – macroionic solutions.

We expect that in the near future, the term of "macroionic solutions" may become a new direction in condensed matter physics and the Chemistry curriculum, paralleling to some other well-established areas such as ionic solutions, polymer solutions, and colloidal suspensions. Discussions on how to incorporate the new results into

Chemistry textbooks are underway with the *Journal of Chemical Education*. A lot of new physical phenomena have been discovered, such as usual thermodynamic and dynamic properties; tuning macroionic charge density via pH and solvent; as well as the bio-membrane like materials formed by pure inorganic species. We have also systematically studied the effects of additional salts, temperature, solvent quality, pH, size and charge density of macroions on the formation of "blackberry."

We are also studying the unique magnetic properties of POM-based giant molecules, which could find new applications in biomedical fields.

SPECIFIC ACCOMPLISHMENTS:

Publications, Reports and Presentations

Tianbo Liu*, Ekkehard Diemann, Huilin Li, Andreas Dress, and Achim Müller, "Self-Assembly in Aqueous Solution of Wheel-Shaped Mo_{154} Oxide Clusters into Vesicles," *Nature*, **2003**, 426, 59.

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.

Guang Liu, Matthew Cons, and **Tianbo Liu***, "The Ionic Effect on Supramolecular Aggregates in Polyoxomolybdate Solution," *J. mol. Liq.*, **2004**, in press.

Guang Liu, Yuguang Cai, and **Tianbo Liu***, "An Automatic and Continuous Dissolution and Precipitation Process in Inorganic Macroionic Solutions," *J. Am. Chem. Soc.*, **2005**, in press.

Tianbo Liu*, Brandon Imber, Ekkehard Diemann, Hartmut Bögge, Guang Liu, Huilin Li, Zhiqiang Chen, Joris van Slageren, and Achim Müller*, "Stepwise Tuning the Charge of Well-Defined Nanoobjects with the Property of Assembling to Vesicles Leads to Charge Dependent Tuning of Size," submitted to *Science*.

Tianbo Liu*, Ekkehard Diemann, and Achim Müller, "Polyoxomolybdate-Based Macroions in Solution: – Novel Sciences Emerge Starting from the Historical 'Blue Waters'" (invited paper), *J. Chem. Edu.*, submitted.

Guang Liu and **Tianbo Liu***, "Thermodynamic Properties of the Unique Self-Assembly of $\{Mo_{72}Fe_{30}\}$ Inorganic Macroions in Salt-Free and Salt-Containing Aqueous Solutions," submitted to *Langmuir*.

The achievements were also widely reported in top scientific public magazines in different countries, such as:

"Singin' the Blue," *Chemistry – American Chemical Society's Award-Winning Publication*, pp.4, Winter **2003**. (USA)

"Magnetic Molecules Take Better Pics – Sharper Scans Out of the Blue," *New Scientist*, vol. 175, issue 2359, pp. 17, September 7, **2002** (U.K.).

"Molybdän und Brombeersoße," *Wissenschaft-online* (German edition of the *Scientific American*), August 28th, **2002**.

"Rounding Up Nanoclusters," *Materials*

Today, January **2004** (U.K.).

"Unique Molecular Structure Offers Insight Into Nanoscale Self-assembly, Solution Chemistry," *Science Daily*, Nov. 6th, **2003** (USA).

"Mo's Better Blues," *Reactive Reports*, Issue #35, **2004** (U.K.).

"Researchers Track New Solute State," *Tcetoday*, September 10th, **2002** (U.K.).

"Old Chemical Enigma Solved," *Popular Mechanics*, pp. 34, December Issue, **2002** (USA).

"Molecular Structure Offers Insight Into Nanoscale Self-Assembly," *Space Daily*, Nov. 7th, **2003** (USA).

"Metal-oxide nanowheels roll up into vesicles," *NanoTechWeb*, Nov. 7th, **2003** (USA).

Science & Technology Trends, Dec. **2003** (Japan).

"Molibdénkékkel," *Nepszabadsag* (Hungary), January 18th, **2003**.

• "Distinguished Oversea Young Scientists Award" from National Science Foundation of China in 2004 (pending final approval).

• Symposium organizer and co-Chair (From polyoxomolybdate to complex ions), 28th International Conference on Solution Chemistry, Debrecen, Hungary, August 23-28th, 2003.

• 14 invited talks.

Four high school students have been working with our group during the summer. They have been very successful in various national competitions.

Brandon 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.

Matthew Cons & Mike Bigesno, *Siemens-Westinghouse* Regional finalist (top 30 in the nation).

LDRD FUNDING:

FY 2003	$ 54,000
FY 2004	$ 95,532
FY 2005 (budgeted)	$ 46,000

Exploratory Sol-Gel Synthesis

Thomas Vogt *03-135*
S. Park

PURPOSE:

The purpose of this project is to develop sol-gel chemical synthesis approaches for novel materials. We are currently focusing on two main areas: (1) the development of successive-ionic-layer-adsorption-and-reaction (SILAR) techniques for thin film synthesis and (2) the exploitation of a novel oxidation/intercalation synthesis route for materials of the $AxMO_2\ nH_2O$ family.

APPROACH:

(1) Successive-Ionic-Layer-Adsorption-And-Reaction (SILAR)

Using the successive-ionic-layer-adsorption-and-reaction (SILAR) method the fabrication of low-cost metal oxide thin films with various particle sizes and thickness can be achieved on a variety of substrates such as Al_2O_3, silicon wafers, plastic or glass. It was recently shown that the SILAR deposition method (Nicolau Y. F. *Appl. Surf. Sci.*, **1985**, *22123*, 1061.) followed by hydrothermal dehydration and annealing is a simple but very flexible method for the low-temperature deposition and crystallization of oxide films.

SILAR deposition is a controlled process of precipitation onto a surface. In its simplest form, only two salt solutions are required. Mixing these solutions must produce a precipitate, which is to become the thin film. A process is generally classified as a SILAR deposition if the film is formed by the sequential addition of individual layers of the complexed ions. In the SILAR deposition the number of dipping cycles and rinsing times controls the thin-film thickness. Furthermore, the pH and concentration of the solutions are also important parameters in controlling the film's thickness and quality. This method is very versatile and can also be used to make gradients within a film by changing the concentration of the aqueous solution as well as to deposit any desired sequence of different metal oxide layers and thereby create multifunctional hydrides. The process can be interrupted and the sample annealed to create a certain morphology and then be re-used as substrate for a subsequent SILAR process thereby varying the morphology of the deposited films.

We have recently shown that the deposition and crystallization of metal oxide films using the SILAR method followed by hydrothermal annealing results in very dense films.

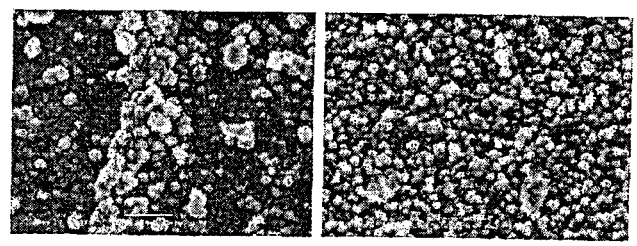


Figure 1: TiO_2 film made using the SILAR process and subsequent furnace (left) or hydrothermal annealing (left).

(2) Oxidation/intercalation synthesis route for $A_xMO_2\ nH_2O$ materials

The extraction of A^+ cations from layered AMO_2 compounds can be accomplished by electrochemical or chemical oxidation using Br_2 or I_2. Alternatively, aqueous solutions of oxidants such as $(NH_4)_2S_2O_8$ (ASO), $Na_2S_2O_8$ (NSO) and $K_2S_2O_8$ (KSO) can also be used. This is an environmentally benign synthesis based on the extraction of the A^+ cations as sulfates.

$$M + Na_2S_2O_8 \xrightarrow[H_2O]{} MSO_4 + Na_2SO_4$$

At the same time as A^+ cations are de-intercalated from AMO_2, water molecules can be intercalated back into the layers between the sheets of edge-sharing MO_6 octahedra.

$$AMO_2 \xrightarrow[H_2O]{\text{oxidant}} A_xMO_2 \cdot yH_2O$$

$$AMO_2 \xrightarrow[H_2O]{\text{oxidant}} A_xMO_2 \cdot yH_2O$$

TECHNICAL PROGRESS AND RESULTS:

(1) The photocatalytic activities as indicated by the H_2 evolution over as-made, hydrothermally annealed, and the furnace annealed TiO_2 films, and a bare Si wafer (size ~ 0.5 x 0.5 cm^2) are shown in Figure 2 (a) – (d), respectively. The H_2 evolution over all films increased linearly with time. The as-deposited film in Figure 2 (a) shows the highest photocatalytic activity of the three films. However, after the photocatalytic experiment for over 50 h, this film was cracked and had partly peeled away from the Si wafer. Comparing hydrothermally treated and furnace annealed (600 °C) TiO_2 films, we find that the hydrothermally treated TiO_2 films show a higher photocatalytic activity and have a much better mechanical stability.

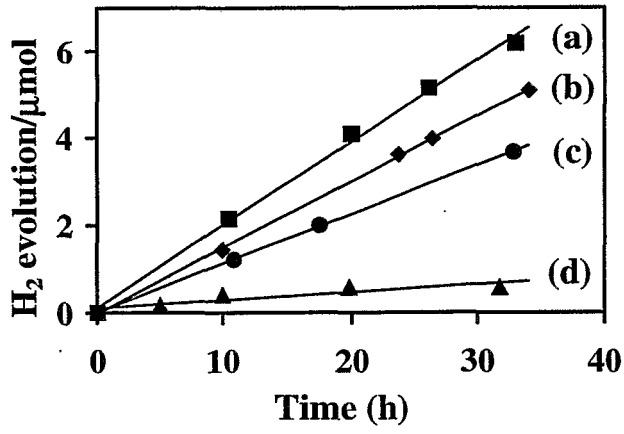


Figure 2. Photocatalytic H_2 evolution over TiO_2 films (700 cycles): (a) as prepared, (b) hydrothermal annealing at 200 °C, (c) furnace annealing at 600 °C and (d) a baseline without TiO_2.

(2) New members of the family of layered metal oxide hydrates $A_{0.3}MO_2 \cdot yH_2O$ with A = Na, K and M = Co, Rh, Ni were prepared from AMO_2 precursors by extracting A^+ cations intercalated between octahedral MO_2 sheets (oxidation) and the simultaneous re-intercalation of water molecules.

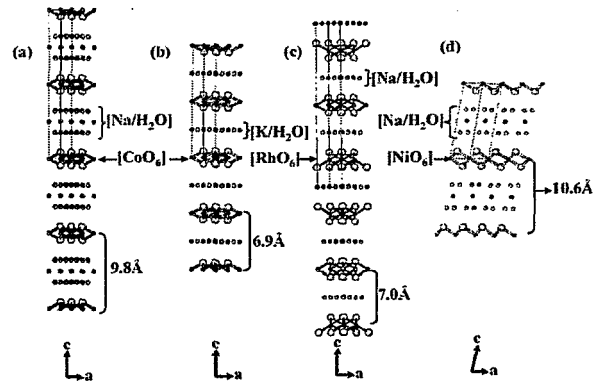


Figure 3. The crystal structures of (a) $Na_{0.3}CoO_2 \cdot 1.3H_2O$, (b) $K_{0.3}CoO_2 \cdot 0.4H_2O$, (c) $Na_{0.3}RhO_2 \cdot 0.6H_2O$, and (d) $Na_{0.3}NiO_2 \cdot 1.3H_2O$.

SPECIFIC ACCOMPLISHMENTS:

Invited talks

"The Chemistry of A_xMO_2 x nH_2O materials." Invited talk in "Transport and Magnetic Properties of Novel Correlated Materials." Pinceton, January 27-28, 2005

Publications

Park, S., Lee, Y., and Vogt, T. (asubmitted) Structural Distortion and Disappearance of Layer Ordering in $Li_xCoO_22H_2O$. **Phys. Rev. B.**

Park, S.; Lee, Y.; and Vogt, T. (2003) *Novel synthesis and high pressure behavior of NaxCoO2yH2O and related phases.* **Phys. Rev. B.** 68, 180505(R).

"The Preparation and Characterization of Photocatalytically Active TiO_2 Thin Films using Sucessive-Ionic-Layer-Adsorption-and-Reaction (SILAR)."
S. Park, E. DiMasi, Y. Kim, P.M. Woodward, T. Vogt
Submitted to Chemistry of Materials

"Synthesis and Structures of Layered $A_{0.3}MO_2$ x nH_2O (A=Na,K and M=Co,Rh,Ni) using an oxidation/intercalation process."
S. Park, V. Solovyov, and T. Vogt
Submitted to Chemistry of Materials

LDRD FUNDING:

FY 2003	$75,000
FY 2004	$81,047

In Situ Soft X-ray Absorption Spectroscopy Studies of Cathode Materials for Thin Film Lithium-Ion Batteries

Won-Sub Yoon *03-137*

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 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 from Massachusetts Institute of Technology (MIT) strongly suggest 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 give 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 in NSLS.

TECHNICAL PROGRESS AND RESULTS:

In the second year of the LDRD (FY2004), we investigated the charge compensation mechanism of cathode materials during electrochemical cycling and expanded the work to mixed transition metal oxide systems. We probed the order in which a particular metal is oxidized and the contribution of oxygen site on the charge compensation process during Li-ion intercalation-deintercalation.

The electronic structure for an electrochemically deintercalated $Li_{1-x}NiO_2$ and $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ electrodes have been investigated intensively with soft XAS at the O K-edge and the metal $L_{III,II}$ -edges using partial electron yield (PEY) and fluorescence yield (FY) detectors.

The Co $L_{II,III}$-edge of pristine $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ shows clear evidence that the Co ions in the compound mostly exist as Co^{3+}. As Li-ion is de-intercalated, the Co 2p spectra do not show any changes in shape or energy position in both the PEY and FY data, indicating that the Co ions in the surface and in the bulk remain mostly unchanged in the Co^{3+} state during charge.

In contrast, it is notable that the Ni $L_{II,III}$-edge XAS spectra for $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$, at various x values, are quite different when obtained in the PEY and FY modes. Ni ions exist mostly as Ni^{2+} at the electrode surface and Ni^{3+} in the electrode bulk in the pristine compound. The major charge compensation at the metal site during charge is achieved by the oxidation of both Ni^{2+} ions at the surface and Ni^{3+} ions in the bulk, while the cobalt ions remain mostly unchanged in the Co^{3+} state. Changes in the spectral weight of pre-edge peaks 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 metal 3d states.

SPECIFIC ACCOMPLISHMENTS:

Refereed Journal Articles:

D. P. Abraham, R. D. Twesten, 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 $LiNi_{0.5}Mn_{0.5}O_2$ Cathode Material during charge," *J. Electrochem. Soc.*, **151**, A246 (2004).

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 $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode System," *Electrochemical and Solid-State Letters*, **7**, A53 (2004).

W.-S. Yoon, M. Balasubramanian, X.-Q. Yang, C.P. Grey, D.A. Fischer, and J. McBreen "A Study on the Electronic Structures of the Electrochemically Li-ion deintercalated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrode System using soft and hard X-ray Absorption Spectroscopy," in preparation.

W.-S. Yoon, X.-Q. Yang, C.P. Grey, D.A. Fischer, and J. McBreen "A Soft XAS Study on the Electronic Structures of the Electrochemically Li-ion deintercalated $LiNiO_2$ electrode System," in preparation.

Presentations:

W.-S. Yoon, M. Balasubramanian, X-Q. Yang, J. McBreen, and C. P. Grey "X-ray Absorption Spectroscopic Studies of $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for Li Rechargeable Batteries," 12th International Meeting on Lithium Batteries, Nara, Japan, 2004.

W.-S Yoon, X.-Q. Yang, K. Y. Chung, and J. McBreen, "X-ray Absorption Spectroscopic Studies of $Li[Ni_xCo_{1-2x}Mn_x]O_2$ for Li Rechargeable Batteries," 206th Electrochemical Society Meeting, Honolulu, Hawaii, USA, 2004.

W.-S. Yoon, X.-Q. Yang, J. McBreen, K. Y. Chung, H. S. Lee, M. Balasubramanianm, and J. Hanson "A X-ray Absorption Spectroscopic study on electrode materials for Li rechargeable batteries," presented (**invited**) at Pohang Light Source, Pohang, South Korea, 2004.

LDRD FUNDING:

FY 2003	$80,000
FY 2004	$46,337

Functional Bulk Mn-Based Nanocomposites

Laura H. Lewis *03-138*
C.-C. Kao

PURPOSE:

The scientific objective of this work is to synthesize and characterize the materials attributes and response of magnetic nanoparticles with a magnetostructural transition. While the magnetostructural transition is often accompanied by an extreme functional response, such as a giant magnetocaloric or colossal magnetoresistive effect, its characteristics remain unknown in nanoparticles. The strategic objective of this work is to enhance the materials synthesis capabilities resident in the Materials Science Department by installation of a commercial Melt Spinner, which is specialized equipment for non-equilibrium solidification synthesis of nanomaterials.

APPROACH:

Novel nanocomposites composed of ferromagnetic nanoparticles of MnBi (or MnSb) embedded in a nonmagnetic matrix of Bi (or Sb) are anticipated to exhibit unusual phenomena such as enhanced ferromagnetism, an improved magneto-optical Kerr effect, a large magnetocaloric effect and a giant magnetoresistive effect. Synthesis was accomplished by melt-spinning the eutectic composition Mn_5Bi_{95} and annealed to create nanorods of MnBi in a coarse-grained Bi matrix (in collaboration with A. R. Moodenbaugh, MSD). Structural characterization of the melt-spun materials has been achieved by standard laboratory x-ray diffraction and high-resolution transmission electron microscopy (HRTEM) (in collaboration with Yimei Zhu). Characterization of the electronic properties was carried out with a Superconducting Quantum Interference Device (SQUID) magnetometry and magnetoresistance measurements (with Qiang Li). Advanced characterization of the phase constitution structural details has been investigated with the synchrotron x-ray (NSLS X7B).

TECHNICAL PROGRESS AND RESULTS:

The commercial Melt Spinner (Edmund-Buhler GmBH, model SC) was installed in December 2003. The rapidly-solidified Mn5-Bi95 alloy was annealed at 530 K for 1 hour and confirmed to exist of isolated, atomically coherent uniform MnBi nanorods of diameter 10 nm and length 30 nm (Fig. 1) A positive temperature coefficient of coercivity was verified, and record coercivity values were measured (~ 40 kOe at 500 K, Fig. 2). A reduction in the Curie temperature of 140 K from the bulk value was recorded, but the spin reorientation maintains the bulk value of 90 K. X-ray diffraction carried out at NSLS Beamline X7B during *in-situ* heating showed that the magnetostructural transition is coincident with abrupt changes in magnetization, coercivity, and crystal structure. A novel particle alignment effect was confirmed under magnetic field heating conditions in which the MnBi nanoparticles rotate to align themselves along an applied 10 kOe magnetic field direction. Annealed ribbons show an extremely high magnetoresistive effect (~400 % at 300 K). Continuation of the structural and electronic characterization, and associated analyses, is planned in FY 2005. In particular, x-ray magnetic circular dichroism (XMCD) measurements will be initiated during that time period.

SPECIFIC ACCOMPLISHMENTS:

Publications:

1) K. Kang, L. H. Lewis, and A. R. Moodenbaugh, "Crystal structure and magnetic properties of MnBi/Bi nanocomposite," *J. Appl. Phys.*, in press.

2) K. Kang, L. H. Lewis, and A. R. Moodenbaugh, "Tailoring the easy magnetization axis of MnBi nanoparticles," in preparation.

3) K. Kang, L. H. Lewis, W.-S. Yoon, and A. R. Moodenbaugh, "Phase evolution in MnBi/Bi nanocomposite," in preparation.

4) K. Kang, L. H. Lewis, W. Hu, Q. Li, and A. R. Moodenbaugh, "Large magnetoresistance of melt-spun MnBi/Bi nanocomposite," in preparation.

Presentations:

1) K. Kang, L. H. Lewis, and A. R. Moodenbaugh, "Crystal structure and magnetic properties of MnBi/Bi nanocomposite," in 49th Conference on Magnetism and Magnetic Materials, Nov. 7-11, 2004, Jacksonville, Florida.

LDRD FUNDING:

FY 2003	$ 28,000
FY 2004	$ 76,906
FY 2005 (budgeted)	$ 42,000

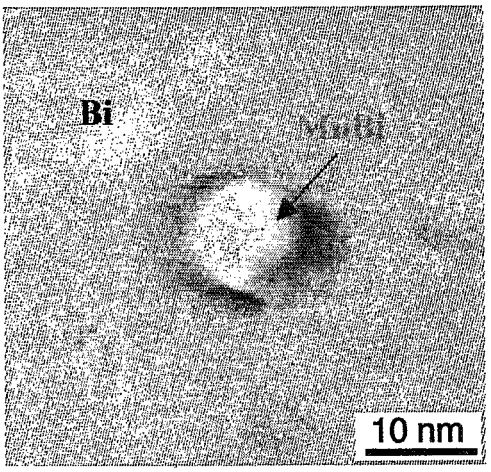


Figure 1. A HRTEM plan-view image of an ex-situ annealed Mn_5-Bi_{95} ribbon.

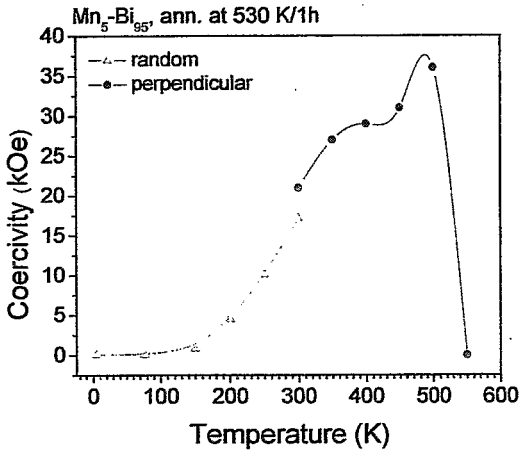


Figure 2. Coercivity dependence on temperature in an ex-situ annealed Mn_5-Bi_{95} ribbon.

Nanostructured Transition Metal Oxides

Lijun Wu *03-144*
M. Suenaga

PURPOSE:

Properties of crystalline solids are not normally classified according to size, but size begins to control and change crystal and electronic structures, and thus fundamental characteristics, at the scale of < 10nm. In this LDRD project, we investigated systematically the crystal and the electronic structures of nano-crystalline cerium and some of the transition metal oxides in order to understand the various factors controlling the changes in the structures from those of the bulk materials.

APPROACH:

In the first part of this project, the cerium and transition metal oxide nanoparticles were synthesized using the technique of thermal evaporation in a helium atmosphere. For observation with transmission electron microscopy (TEM), the particles were collected onto the lacy-carbon-coated side of the copper grids during the course of evaporation. In the second part, we also compared the structures of the nanoparticles made by different processes.

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. In general, TEM mode was used to obtain high-resolution images and diffraction patterns for the measurements of lattice parameter, while the scanning transmission electron microscope (STEM) mode was employed to obtain electron energy-loss spectra (EELS) for individual particles. The probe size in the STEM mode 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 and R. Klie (BNL); D.A. Fischer (NIST); M. Yin and Peter Russo (Columbia University); M. Choi (Seoul Nat'l Univ. Korea).

TECHNICAL PROGRESS AND RESULTS:

In FY 2003, we 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. We have acquired a series of EELS spectra over a range of particle sizes of CeO_{2-x} nanoparticles.

In FY 2004, we measured the lattice parameters over a range of particle sizes for CeO_{2-x} nanoparticles by high-resolution images. We also measured the distributions of Ce^{3+} and Ce^{4+} ions across the diameters of CeO_{2-x} particles with diameters of approximately 13nm. It indicates that there are non-uniform distributions of Ce^{3+} and Ce^{4+} (with accompanying oxygen vacancies), which can be approximated as a core-shell structure with a thin $CeO_{1.5}$ shell and a CeO_2 core. Based on this core-shell structure, a

micromechanical model was used to calculate the lattice parameters of nanoparticles over the particle size range. Fig. 1 shows the measured and calculated lattice parameters over the particle size range. They are in a good agreement. Both our results and those reported by Tsunekawa et al.[1] and Zhang et al.[2], show that the lattice parameter of CeO_{2-x} nanoparticles increases with decreasing particle size. However, our particles showed larger lattice expansions than that reported by Tsunekawa et al. and Zhang et al. The differences were attributed to the different amount of Ce^{3+} ions in small CeO_{2-x} particles, which appeared to be due to the differences in processing methods. Particularly, those particles made by Zhang *et al.* were octahedral in shape with (111) planes as the terminating surface which was well-known as the most stable CeO_2 plane against the formation of surface oxygen vacancies. Hence, it is more difficult to form a $CeO_{1.5}$ layer on this type of particle than those having other terminal planes.

In conclusion, the rate of the valence reduction and the lattice expansion is strongly dependent on the processing methods of the particles. Those particles which have less stable terminating surface planes are more susceptible to the reduction and the expansion. These are likely to be more chemically active and have greater catalytic properties.

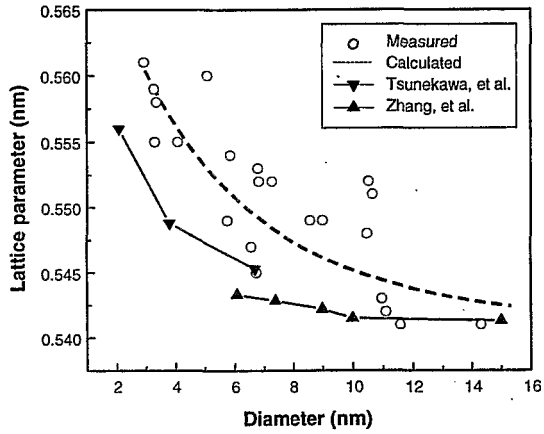


Figure 1. Lattice parameter of CeO_{2-x} particles as a function of the particle size. The open circles were measured from the high-resolution images. The dashed line is the calculation based on the micromechanical model. The lattice parameters reported by Tsunekawa, et al. and Zhang, et al. are also shown for comparison.

Also, in FY 2004, the TiO_2 nanoparticles, which were prepared by the thermal evaporation method, and those by different processes from that of Choi and Aldrich were also investigated. In addition, we have analyzed the lattice parameters for Cu_2O and Mn_2O_3 nanoparticles (from Yin and O'Brien). Unlike CeO_{2-x} nanoparticles, the lattice parameter of Cu_2O nanoparticles decreases with decreasing particle size. Mn_2O_3 nanoparticles have a tetragonal lattice, decreasing with particle size, and the lattice parameter a increases, while c decreases.

References:

1) S. Tsunekawa, et al., Phys. Rev. Lett. **85**, 3440 (2000).
2) F. Zhang, et al., Appl. Phys. Lett. **80**, 127 (2002).

SPECIFIC ACCOMPLISHMENTS:

A presentation titled "Electron Energy Loss Spectroscopy of CeO_{2-x} Nanoparticles," was given by Lijun Wu at the Microscopy and Microanalysis 2003 Meeting, Proceedings 820CD.

"Oxidation state and lattice expansion of CeO_{2-x} nanoparticles as a function of particle size," L. Wu et al., Phys. Rev. B 69, 125415 (2004).

LDRD FUNDING:

FY 2003	$40,000
FY 2004	$76,347

Radio Wave Detection of Ultra High Energy Cosmic Rays

Helio Takai *03-151*

PURPOSE:

This project seeks the detection of ultra-high energy cosmic rays via radio (radar) detection. It is well known that micro-meteors when vaporized in the upper atmosphere produce ionization trails that reflect radio waves in the 30-100 Mhz range. Ultra-high energy cosmic rays with energy larger than 10^{18} eV produce ionization densities similar to micro-meteors; and hence their detection via radio (radar) should, in principle, be possible. To prove the concept, an experiment where a radio echo is detected simultaneously with muons produced in the shower is being built. If proven successful a dedicated experiment can be built to cover an area near to 10^6 km^2 at a reasonable cost for the study of ultra-high energy cosmic rays.

APPROACH:

In recent years cosmic rays of energy larger than 10^{20} eV have been detected. The origin and nature of the acceleration mechanism that can accelerate particles to such high energies is unknown. To put in perspective these energies are four orders of magnitude larger than what the Large Hadron Collider, scheduled to be operational in 2007, will accelerate. What are the acceleration mechanisms that can accelerate particles at these extreme energies? What sources of energy are available to accelerate particles at these energies? To study this problem large area detectors are required due to the very low event rate. The largest detector now under construction, the Auger observatory, will cover an area of 3,000km^2. Radar allows for the construction of detectors with coverage of the order of 10^6 km^2. This project seeks the detection of Radio waves from commercial transmitters, e.g. TV stations, in coincidence with compact shower detectors. Because of the distances involved, detection sites will be located far apart. Each detection site will acquire data independently and register the detection time using a Global Positioning System (GPS) clock. All the event times will be scanned off line and coincidences sought.

We collaborated in this project with SUNY Stony Brook (M. Rijssenbeeck), the Suffolk County Community College (B. Warasila, T. Breeden and M. Inglis), and ten high school physics teachers from Long Island and Maryland.

TECHNICAL PROGRESS AND RESULTS:

Two radio stations were completed. The sites are at BNL and Suffolk County Community College. A week long run was performed during the August 2004 Perseid meteor shower. The coincidence data allow us to reject local noise from buildings and surroundings. The preliminary data analysis shows a multitude of coincidence events and features of the meteor shower can be clearly seen.

The data acquisition went through a complete redesign during this period. It was noted that few samples were missing with the first data acquisition system. The adoption of real-time operating systems, faster disks and proper handling of interrupts led to a robust data acquisition. In addition, the GPS information is now encoded with the event for proper timing. The timing information can be recovered within ± 5 μs. This value is a little larger than the desired ± 1 μs, but given the lower event rate it should be adequate for our initial purposes.

A survey of GPS clocks was carried out. After the survey it became clear that GPS clock performances vary significantly as function of vendors. We have selected a GPS clock that can be used for both compact shower detectors and radio detection stations. This GPS made by Spectrum Instruments has an internal accuracy for time tagging of 100ns.

We have successfully completed the construction of compact shower detectors that are now being installed in high schools participating in this project. GPS clocks are also being installed, and we expect them to become on-line shortly. The initial data-taking phase is expected for January 2005, with the data from scintillators manually uploaded to BNL.

Progress in the understanding of the radio signal duration and shape was done. An experiment to measure the lifetime of free electrons in air was built at the BNL NSLS. The results obtained are very encouraging and demonstrate that radio detection should be possible. To complete the experiment we intend to map the lifetime for the pertinent altitudes where we expect high ionization.

We have involved in all activities students at the Masters level from the SUNY - Stony Brook, University of Rio de Janeiro (Brazil), and Cornell University.

The understanding of the radio signal and how it will present for cosmic rays has been one of our priorities. A toy model based on all the acquired experience has been built. This model allows us to estimate important parameters for the search of candidates. It also allows for the design of custom radios for the present problem.

SPECIFIC ACCOMPLISHMENTS:

We have presented results of our experiment at the following conferences:

Radio Wave Detection of Ultra High Energy Cosmic Rays, D. Damazio, T. Falcone, N. Mehta, and H. Takai, Spacepart 2003, in Washington, DC, December 11-13, 2003

The Radio Detection System Data Acquisition System, D. Damazio and H. Takai, Nuclear Science Symposium in Rome, Italy, October 16-24, 2004

Currently, we are working on a proposal for the National Science Foundation for the continuation of this project. This proposal will be submitted jointly with SUNY- Stony Brook.

LDRD FUNDING:

FY 2003	$100,000
FY 2004	$123,923
FY 2005 (budgeted)	$ 25,000

Generation of Coherent, Femtosecond, High Brightness VUV and X-ray Beams Using High Order Harmonic Conversion

Triveni Srinivasan-Rao *03-161*

PURPOSE:

In recent years there has been significant progress in increasing the brightness of high harmonic generation in the Vacuum ultra violet (VUV) and the X-ray ultra violet (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 ~10^{13} W/(cm^2 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. 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 for 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.

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 μJ, 10 fs photon pulses at 800 nm with Bessel function intensity distribution, (2) development of high repetition rate gas jet, (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 femtoseond 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. To characterize the high harmonic radiation the VUV radiation is down converted to the visible on a sodium-salicylate coated vacuum window, and the fluorescence signal is detected by a PMT. A differential pumping system maintains the gas jet at the required pressure while preserving adequate vacuum in the spectrometer.

TECHNICAL PROGRESS AND RESULTS:

Phase 1 was completed in the first year of the project. The Ti:sapphire regenerative amplified system used in the project 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 0.4 mJ, pulse duration of 200 fs and repetition rate up to 10 kHz. A pressure vessel capable of supporting a 2-atmosphere pressure was constructed to house a 70 cm long hollow-glass capillary tube of 125 μm in diameter. The laser beam was coupled into the high pressure vessel and the spatial profile of the beam was modified from Gaussian to Bessel function 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. Significant spectral broadening, mostly due to self phase modulation, was observed for different noble gases at various pressures. The broadest spectrum, >150 nm, was achieved using Xe gas at 20 psi. Such a large spectral content when compressed appropriately would support a pulse width of ~5 femtosecond in duration. Figure 1 shows the linear dependence of the spectral broadening on gas pressure and the length of the hollow capillary tube. It is clear that a longer capillary tube and higher gas pressure are essential to spectral broadening leading to shorter compressed optical pulses. 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.

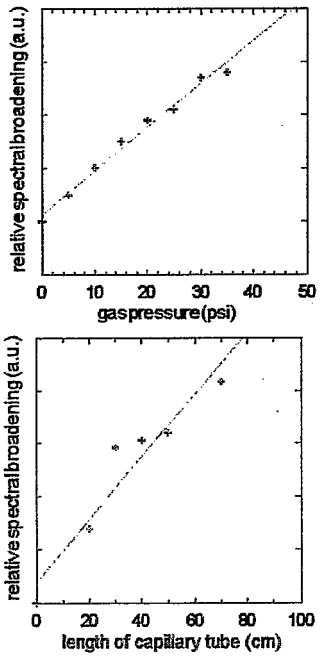


Figure 1. Dependence of the spectral broadening on gas pressures (left) and length of the capillary tubes (right).

A high repetition rate, piezo-driven, pulsed, gas jet was deigned and built. Figure 2 shows the profile of the gas jet measured using a HeNe laser beam. A vacuum spectrometer system consisting of the gas jet, differential pumping stages, vacuum spectrometer capable of maintaining 10^{-4} Torr with the gas jet operating, and VUV sensitive photo multiplier has been built and

tested. The photo multiplier has been calibrated at 160 nm, the fifth harmonic of the 12 fs Ti:sapphire laser.

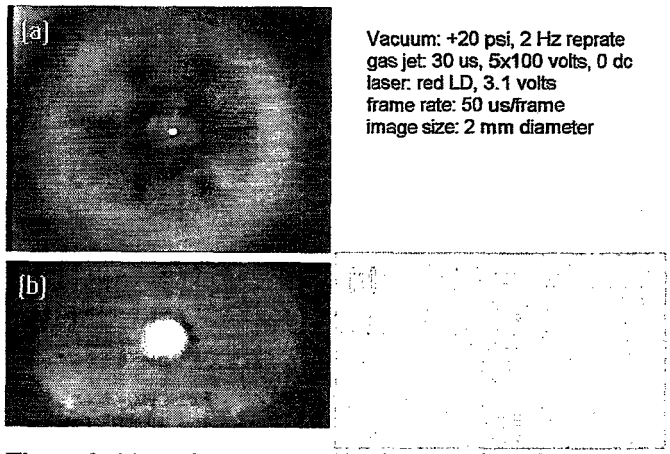


Figure 2. (a) gas jet aperture, (b) Close up of gas jet aperture, (c) Fringe pattern formed by gas jet back illuminated using a HeNe laser.

A focusing lens of 25 cm was used to focus the amplified laser beam onto the gas jet operating at various gas pressures. The observed harmonic radiation is displayed in Figure 3.

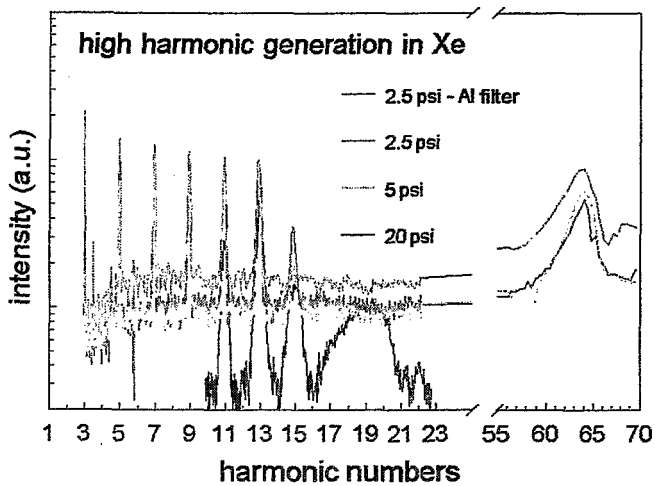


Figure 3. Harmonic radiation generated at different gas pressures. All but one signal trace (—) was measured with an aluminum filter to block the fundamental radiation.

As can be seen from Figure 3, distinct harmonics up to the 15th harmonic were observed, beyond which dephasing between the fundamental and the harmonic tends to broaden the spectral width of the signal. The signal at 20 eV (13th harmonic) corresponds to an estimated ~10^6 photons/pulse, assuming the QE of the fluorescent window of the detector to be 1% and the throughput of the monochromator to be 20%. When the laser amplifier and the gas jet are driven at a kHz repetition rate, this corresponds to 10^9 photons/sec, which is one of the goals of the project. It is worth noting that the signal amplitudes are nearly constant for all the harmonics up to the 13th. The highest photon energy observed was 36 eV at the 23rd harmonic, as anticipated by the cutoff energy of the monochromator system. Presently, we are investigating the signal seen beyond the 60th harmonic. We would also be coupling the laser light into the gas-filled capillary tube prior to focusing on the gas jet to modify the spatial profile, decrease the pulse duration, increase the intensity of the fundamental, and to improve the intensity and the order of the harmonic radiation.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2003	$ 130,000
FY 2004	$ 139,719

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 superconductivity with approximately double the critical temperature T_c of other intermetallics. Because interband electron scattering is almost completely prohibited, it may be tuned to produce high upper critical fields and desirable properties while preserving the high T_c. New synthesis techniques to manipulate vacancies and alloying elements in advanced intermetallics are being developed by this project.

APPROACH:

MgB_2 has been the first material of focus. Considerable effort has been devoted to understanding what the effects of alloying might be, given that carbon alloying drives the upper critical field $\mu_0 H_{c2}$ from ~18 to ~35 tesla and above the ~30 T limit of Nb_3Sn. We developed a special apparatus to control Mg volatility during 2003, and during the past year we used this apparatus to prepare MgB_2 alloyed with carbon, sodium, lithium, aluminum, and oxygen. We were also able to rule out alloying with silicon. With the expertise of R. Klie, these samples were then fed to advanced electron microscopy tools in the Center for Functional Nanomaterials. Coordinated electromagnetic measurements and heat capacity give us a picture of how the electronic structure and electron scattering both evolve as a function of doping.

We also studied MgB_2 and Nb_3Sn using high-energy ball milling to intentionally blend components at the nanoscale prior to reaction and incorporate high densities of atomic defects. This produces a high density of interfaces and strains, which drives down T_c, but can drive up H_{c2} faster. Coordinated x-ray diffraction with electromagnetic property characterization then gives us a picture of how potent site disorder is for improving high-field properties.

Lastly, we began studies of boron suboxide and suboxide carbide compounds. Analogous to C_{60} compounds, these are based on B_{12} icosahedra and can exhibit a range of behavior when carbon and oxygen are substituted. Doping with alkali and transition metals, e.g. ZrB_{12}, allows the electron Fermi level to be changed, giving properties that can be tuned from semiconducting to metallic and superconducting.

TECHNICAL PROGRESS AND RESULTS:

This project was begun in mid-FY2003. A new postdoc, Antonio Zambano, was hired in July 2004. Using this project as a seed, we led a successful effort to establish a DOE-BES Center of Excellence for the Synthesis and Processing of Advanced Materials project. CSP projects have a high profile in BES, being part of the technology steering activities. Unfortunately, the entire CSP program was cancelled at the start of FY2005.

Reactions of Mg with B_6Si were used to show that good properties can be obtained for low-temperature reactions. This study also ruled out any alloying of Si into MgB_2,

which was reported for wires made with SiC additives. The benefit of SiC implied by our work is that carbon alloying and the formation of Mg_2Si precipitates for flux pinning.

Reactions of Mg with B_4C produced samples with various carbon doping. Scanning transmission electron microscopy with electron energy loss spectroscopy (STEM-EELS) showed that carbon's extra electron fills the critical hole states in the planar boron bands. Since this could drive the σ band toward a metal-insulator transition, it thus explains why carbon is a potent source of electron scattering and also why T_c falls rather quickly with increasing carbon content. Curiously, the hybrid π band, the second of the two bands of the unique 2-band superconductivity mechanism, was almost unaffected by adding carbon.

Reactions of Mg and $NaBH_4$ or $LiBH_4$ with B produced alkali-metal doped samples. Here, the added holes showed up in STEM-EELS as a clear increase in the isotropic boron π band hole states, while the σ states showed little change. Al-added samples showed opposite effects, both a decrease of the π band hole density of states and slight changes in the σ band states. The EELS studies suggest that the electrons or holes in this group enter primarily the π band and do not strongly perturb the stronger σ band. This may explain why neither Al or Alkali metals produce strong electron scattering and high H_{c2}.

Taken together with the Alkali metal and carbon doping results, a picture of non-rigid band filling in MgB_2 is emerging. We are presently trying to model how changes in the lattice parameters, which change the density of states, might also affect the contribution of electrons or holes to the σ or π band.

The strong site disorder produced in Nb_3Sn compounds by ball milling caused the T_c to fall, which could be reversed by annealing. While these changes were expected, we also found that limiting the degree of disorder recovery led to a good blend of strong scattering and moderate T_c reduction. This improved the upper critical field by about 5 T at low temperature, a result similar to the huge increase reported recently in $PbMo_6S_8$. In MgB_2, similar results are emerging. However, interband scattering, which reduces T_c, seems to be more difficult to remove, which suggests it is very sensitive to site order.

SPECIFIC ACCOMPLISHMENTS:

Publications:

- L.D. Cooley, Kyongha Kang, R. F. Klie, Qiang Li, A. M. Moodenbaugh, and R. Sabatini, "Low-temperature synthesis of MgB_2 from B_6Si," Supercond. Sci. Technol. **17** (2004) 942.
- L.D. Cooley, R. Klie, Qiang Li, A. Moodenbaugh, R. Sabatini, and A. Zambano, "Evidence for non-rigid band filling in electron and hole-doped MgB_2," in preparation.

LDRD FUNDING:

FY 2003	$ 88,000
FY 2004	$ 90,577
FY 2005 (budgeted)	$ 71,000

Femtosecond Photoinitiated Nanoparticle Surface Chemistry

Nicholas Camillone III *04-011*

PURPOSE:

The goal of this project is to bring together the ultra-fast and the ultra-small in order to understand the physics behind the unique chemistry of nanostructured materials. Towards this end we aim to apply techniques developed to probe the chemical dynamics of 2-D planar surfaces with femtosecond time resolution to the study of the chemistry of molecules adsorbed on supported nanoparticles. Thus, the technical objective of this project is to develop femtosecond laser-based capabilities that are new to BNL to probe surface chemical dynamics on nanoparticles in real time. The proposed work intersects three ongoing efforts at BNL: the Ultrafast Optical Sources Cluster in the Center for Functional Nanomaterials, the Laser-Electron Accelerator Facility, and the Catalysis on the Nanoscale Program. Success of this project will form a nucleus for discovery in an important area with the promise of continued growth in a number of different venues at BNL.

APPROACH:

About ten years ago a new class of surface chemical processes was demonstrated[1] and has very recently begun to be exploited to study reaction dynamics on 2-D planar surfaces.[2] These processes involve non-adiabatic excitation driven by the absorption of femtosecond light pulses. However, very little has been done to explore these phenomena on nanoscale materials,[3] where size-dependent properties are expected to impact the dynamics of surface chemical transformations.[4] In particular, for photoinduced chemistry on supported metal nanoparticles, spatial confinement of ballistic electrons, size-dependent electronic structure[5] and the sensitivity of electron-phonon coupling to surface thermal vibrations[6] are expected to significantly affect hot electron lifetimes in small nanoparticles. Furthermore, enhancements in photoelectron yield from nanoparticles have been indicated.[7] These effects are expected to dramatically impact photochemical cross sections and dynamics of adsorbates at nanoparticle surfaces.

We aim to explore size-dependent behavior of the photoinduced chemistry and chemical dynamics as the size of the nanoparticles is varied through the size regime spanning the non-metal to metal transition. The experimental approach we will employ is known as the two pulse correlation technique.[2, 8] In such an experiment, the excitation pulse (800 nm, ~ 100 fs, ~ 1 mJ/cm^2) is split into two pulses which are directed to impinge upon the surface separated in time by a variable delay. The photoinduced desorption yield is measured by a quadrupole mass spectrometer (QMS), as shown in Fig. 1. Because the relaxation times of the electronic temperature and the lattice temperature differ by an order of magnitude, the

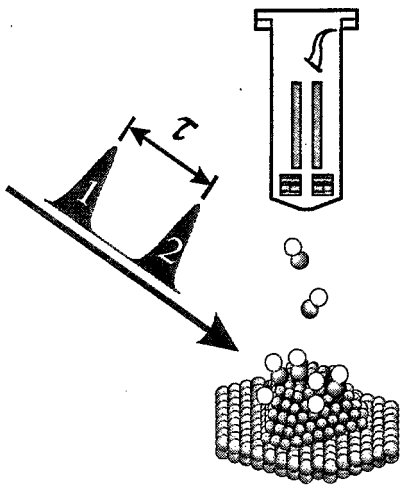


Figure 1. Schematic diagram of the two-pulse correlation measurement.

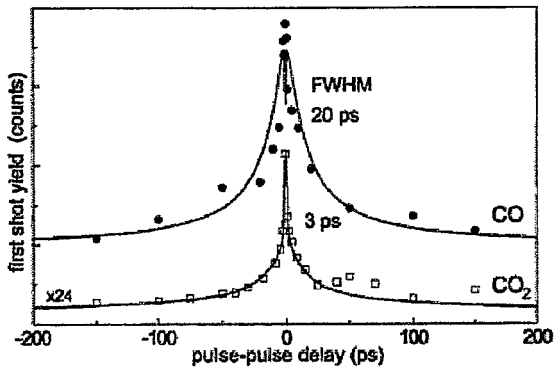


Figure 2. Subpicosecond-resolution two-pulse correlation measurements illustrating the distinct responses for an electron-mediated process (CO oxidation by electronically stimulated O) and a phonon-mediated process (CO desorption). (From Ref. 2.)

time dependence of the yield depends upon the desorption mechanism. When electronic coupling dominates the processes, the desorption yield correlation width approximates the relaxation time of the electronic temperature, showing a sub-picosecond to picosecond response. For a phonon-mediated process, desorption remains efficient for much longer delay times, and the yield shows a much longer (~ 20 ps) correlation width. Figure 2 shows data taken from the work of Bonn *et al.* that exemplifies the distinct timescales for these two types of processes on a 2-D planar surface.[2]

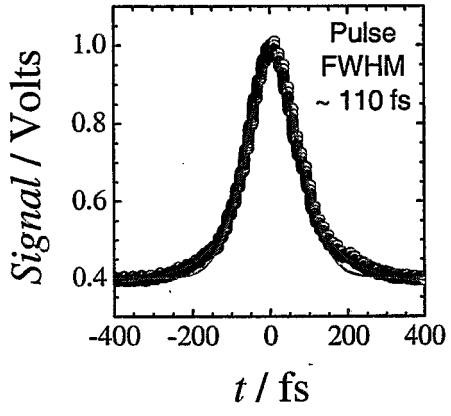


Figure 3. SHG autocorrelation measurement from which a pulse width of ~ 100 fs is extracted for the amplified 800 nm pulses.

Our pursuit of such time-resolved dynamical measurements on nanoparticles will require establishment of a high power (~ 1 mJ) source of 100 fs laser pulses, construction of an optical train to manipulate the pulses and introduce them into an ultra-high vacuum environment, development of an ion counting scheme and control software to detect photodesorbed species with the QMS, and development of the capability to deposit nanoparticles on a solid support.

Conception of this project and assembling the diverse elements of the experiment has involved the collaboration of Alex Harris (Chemistry) and Jim Misewich (Materials Science). In addition, important components of the effort have been enabled by a collaboration with M. White (Chemistry BNL and SUNY Stony Brook).

TECHNICAL PROGRESS AND RESULTS:

During fiscal year 2004 several important milestones towards achieving our stated goals have been reached:

• A regenerative amplifier, on loan from SUNY Stony Brook (courtesy of M. White) was relocated to our laboratory at BNL. Laser interlocks and the laboratory Standard Operating Procedure were updated as required. Initial characterization of the output pulses was made using a single-shot autocorrelator on loan from Spectra Physics (see Fig. 3).

• Research into a more advanced tool for spatial, spectral and temporal pulse diagnostic was completed and a device (using the FROG – frequency resolved optical gating – method) was identified and purchased for this purpose.

• The train of optical and optomechanical components necessary for manipulating the

pulses and introducing them into the UHV chamber was designed. These components, including a translation stage for a computer-controlled optical delay line, were purchased.

• An ion counting scheme for detecting molecules and molecular fragments ejected from the surface as a result of exposure to the amplified pulses was devised. Control and data acquisition software was developed. Initial tests involving measuring current pulse outputs by the electron multiplier in the QMS and scanning the mass setting of the QMS under computer control were completed (see Fig. 4).

Continuation of this work during the upcoming fiscal year is anticipated. Milestones for next year include: installing the FROG device, performing proof of method experiments for photoinduced desorption of O_2 and CO from Pd(111), and installing an evaporative metal source for physical vapor deposition (PVD) growth of supported nanoparticles.

Our goal is to explore the size-dependence of the desorption dynamics of molecular adsorbates from nanometer scale metal particles. Goodman and coworkers have shown that Au and Pd nanoparticles can be grown on rutile, TiO_2, with a relatively narrow size dispersion by PVD with mean particle diameters on the order of 1 to 50 nm.[5, 9] This size regime is of interest because the reactivity of the particles for the catalytic oxidation of CO shows a marked peak for particles approximately 3 nm in diameter, and this peak in reactivity coincides with the non-metal to metal transition.[10, 11] Our aim is to measure the desorption dynamics of CO from nanoparticle assemblies as a function of nanoparticle size to begin to probe the chemical dynamics behind the marked size-dependence of the reactivity of this model catalytic system.

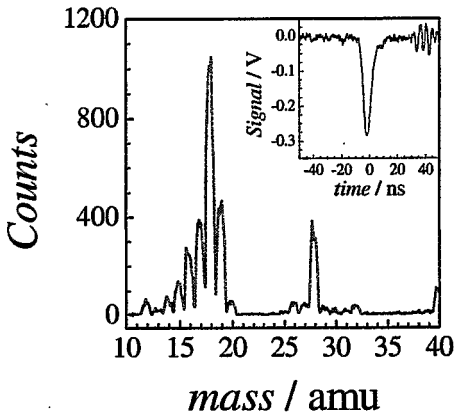


Figure 4. Mass spectrum recorded using the ion counting scheme and newly written QMS control software. Inset: current pulse output of the QMS continuous dynode electron multiplier.

SPECIFIC ACCOMPLISHMENTS:

Strategic Accomplishments

• Based in part on extension of this LDRD work, a proposal for "Ultrafast Investigations of Surface Chemical Dynamics" was made at the DOE Chemical Sciences Review of the BNL Chemical Physics Program in October of 2003. The proposal is approved for funding, with initial funds available in FY 2005 and increasing in FY 2006.

• As a result of the success of the October 2003 proposal to DOE, we have formed a new Surface Chemical Dynamics Group. The group includes M. White and R. Beuhler, A. Harris, and N. Camillone (all BNL Chemistry).

• Inclusion of a postdoctoral research associate in the original FY 2004 budget for this LDRD enabled the successful search for a new hire. The new research associate was hired and starts in November 2004. In his first year he will collaborate on this LDRD effort.

LDRD-Related Presentations (FY 2004)

- *"Femtosecond Photoinitiated Nanoparticle Surface Chemistry,"* N. Camillone III, oral presentation at the *Mid-Year Review of LDRD Projects* (BNL, May 3, 2004).

- *"Ultrafast Investigations of Surface Chemical Dynamics,"* N. Camillone III, oral presentation at the *DOE Chemical Sciences Review of the BNL Chemical Physics Program* (BNL, October 28, 2003).

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LDRD FUNDING:

FY 2004	$ 79,532
FY 2005 (budgeted)	$ 121,000

Chirped Pulse Amplification at the DUV-FEL

Li Hua Yu *04-013*

PURPOSE:

We propose to investigate the Chirped Pulse Amplification (CPA) by a Free-Electron Laser (FEL) at the DUV-FEL facility. In a seeded FEL, when the seed laser is chirped and the electron bunch is also chirped accordingly, the output radiation is also amplified and chirped. When the chirped output is compressed by an appropriate optical system, the output can have very short pulses with very high peak power.

APPROACH:

Our approach is to use the High Gain Harmonic Generation (HGHG) process to carry out CPA at the DUVFEL. The HGHG approach utilizes a laser-seeded FEL to produce amplified, longitudinally coherent, Fourier-transform-limited output at a harmonic of the seed laser. Since the output wavelength is reduced by the harmonic number but with the same percentage of chirp as the seed, the pulse length is also reduced by the harmonic number when compared with the bandwidth limited seed pulse length. This makes it possible to achieve an ultra-short pulse length with high peak power. With the existing laser technology of 6 % bandwidth (most updated technique allows for 9% bandwidth), with the possible energy chirped chirp range of 3% at the DUV-FEL, our calculation showed that it is possible to achieve 7 fs with 6 GW peak power at 266 nm. Recently, we have carried out the HGHG experiment at 266 nm using a Near Infra-red Scalable Undulator System (NISUS) undulator at the DUV-FEL. The results agree with the theory very well. Short pulse amplification is also an important part of the cascaded HGHG experiment to achieve x-ray FEL. Here, we plan a first CPA experiment to confirm this principle, with the ultimate goal of providing an intense, highly coherent ultra-short pulse source of hard x-rays.

TECHNICAL PROGRESS AND RESULTS:

During FY 2003-2004, we have made significant progress towards achieving CPA in FEL.

Since we have achieved stable HGHG output at 266 nm using an 800 nm seed, we started to chirp the seed and the electron beam energy within the electron bunches. By varying the energy chirp, we changed the matching between the seed and the electron bunch, and in the meantime, we measured the bandwidth. The results showed a maximum bandwidth at a certain chirp rate of the electron bunch, and the bandwidth is 1.5nm, quite close to the theoretically expected maximum bandwidth achievable, i.e. 1.8 nm. This gave us confidence for the desired CPA.

We then proceeded to install the SPIDER (Spectral Interferometry for Direct Electric-Field Reconstruction) to measure the phase distortion of the HGHG output. We were able to carry out the SPIDER measurement on the HGHG output, and start to vary the chirp and change the bandwidth. The results showed the output is chirped agreeing with theory, and hence should be able to be compressed.

SPECIFIC ACCOMPLISHMENTS:

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

We are seeking funding from the Joint Technology Office on high-energy free electron lasers, which is based on the recent works on HGHG.

Non-refereed publications:

- H. Loos, A. Doyuran, J. B. Murphy, J. Rose, T. Shaftan, B. Sheehy,Y. Shen, J. Skaritka, X.J. Wang, Z. Wu, L.H. Yu, "ELECTRO-OPTIC LONGITUDINAL ELECTRON BEAM DIAGNOSTIC AT SDL," PAC 2003.

- T.Shaftan, Z. Huang, A. Doyuran, L. Carr, W.S. Graves, C. Limborg, H. Loos, J. Rose, B. Sheehy, Z. Wu, L.H. Yu, "Experiments with electron beam modulation at the DUVFEL accelerator," Volume 528, Issues 1-2, 1 August 2004, Pages 397-401.

- J. Rose, B. Podobedov, J. Murphy, T. Shaftan, B. Sheehy, X.J. Wang, L.H Yu, "A SCRF Linac as a FEL Driver and Storage Ring injector," PAC2003.

- T. Shaftan, L.H.Yu, "HGHG with Variable Wavelength," BNL-72034-2004-JA.

Refereed publications:

- Adnan Doyuran, Louis DiMauro, William Graves, Richard Heese, Erik D. Johnson, Sam Krinsky, Henrik Loos, James B. Murphy, George Rakowsky, James Rose, Timur Shaftan, Brian Sheehy, Yuzhen Shen, John Skaritka, Xijie Wang, Zilu Wu, and Li Hua Yu, "Experimental study of a high-gain harmonic-generation free-electron laser in the ultraviolet," Phys. Rev. ST Accel. Beams 7, 050701 **(2004).**

- 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).

- Adnan Doyuran, Louis DiMauro, Richard Heese, Erik D. Johnson, Sam Krinsky, Henrik Loos, James B. Murphy, George Rakowsky, James Rose, Timur Shaftan, Brian Sheehy, Yuzhen Shen, John Skaritka, Xijie Wang, Zilu Wu, Li Hua Yu, "Preliminary Chirped Pulse Amplification of HGHG-FEL at DUV-FEL Facility in BNL," NIM, A,Volume 528, Issues 1-2, Pages 467-470 (2004).

- L.H. Yu, "R&D experiments at BNL to address the associated issues in the Cascading HGHG scheme," Proceedings of International FEL Conference, 2004, Trieste, Italy.

- Z. Wu, H. Loos, Y. Shen, B. Sheehy, E. D. Johnson, S. Krinsky, J. B. Murphy, T. Shaftan, X.-J. Wang, L. H. Yu, "Spectral Phase Modulation and chirped pulse amplification in High Gain Harmonic Generation," Proceedings of International FEL Conference, 2004, Trieste, Italy.

LDRD FUNDING:

FY 2004	$ 78,404
FY 2005 (budgeted)	$120,000

Overcoming Coherent Instabilities at Medium-Energy Storage Rings

Jiunn-Ming Wang *04-025*

PURPOSE:

The coherent instability is a challenging problem at NSLS-II because of the designed high peak current and small momentum compaction. Particularly, the transverse mode coupling instability (TMCI) excited by the minigap undulators (MGU) is expected to be particularly serious. As is well known, this instability is one of the limiting factors of the beam current in many light sources throughout the world. Indeed, calculations indicate that the beam would be quite unstable if we adopt an APS 5 mm MGU for NSLS-II; the threshold bunch current would be 0.25 mA compared to the designed bunch current of 0.75 mA. The purpose of this LDRD is to explore the best ways to minimize the coherent instability in the NSLS-II ring.

APPROACH:

(I) Compute and understand the beam impedance $Z(\omega)$ of the ring components. If necessary, modify the designs of the individual component in order to reduce the corresponding impedance; special attention is paid to vertical impedance $Zy(\omega)$ of MGU.

(II) Theoretical study to estimate impact of the measured impedance on the NSLS-II ring coherent instability.

(III) Study the feasibility of the TMCI feedback damper (FB).

(IV) Bench measurement of Z to complement the knowledge we gained about Z by computer computation.

The collaborators of this work include A. Blednykh, S. Kramer, J.B. Murphy, B. Podobedov and G. Rakowsky.

TECHNICAL PROGRESS AND RESULTS:

Progress during FY 2004:

(1) We studied both longitudinal and transverse coupled bunch instabilities. Conclusion:
(a) The beam is stable against the resistive wall longitudinal coupled bunch instability.
(b) The beam is unstable against the corresponding transverse instability. Installation of the transverse coupled bunch feedback damper is suggested.

(2) The longitudinal microwave instability due to coherent synchrotron radiation impedance is shown to be stable because of shielding.

(3) We have written computer program based on an asymptotic expansion of the Ruth-Wang integral equation in order to study TMCI.

(4) A computer program is written based on a theoretical formulation of the TMCI FB in order to compare the usefulness of various schemes of the TMCI FB. The present program and the program (3) mentioned above are indispensable tools in carrying out this LDRD project.

(5) Achieved designs of MGU with the effective impedance a factor of 5 ~ 10 smaller than that of the corresponding APS MGU.

(6) The discrepancy between Yokoya prediction and the computer computation for the long-wavelength limit of the transverse impedance is successfully explained by invoking the presence of trapped low frequency thermo electric (TE) resonances.

Elaboration on item (4) above:

By adjusting the phase between the beam signal pickup and the kicker, a TMCI FB can be operated either capacitively or resistively. In either kind of operation, the FB system is expected to be effective against TMCI. However, it is of great interest to know whether the capacitive or the resistive FB is more effective. In 1987, Steve Myers et al of CERN did a series of experiments at PEP in order to answer this question. The experimental results indicated that the capacitive FB is more effective at lower current and the resistive FB is more effective at higher current.

In 1997, John Byrd et al did similar experiments at ALS and found the resistive FB to be more effective for all currents. The different conclusions of these two groups have for a long time elluded explanations.

Recently, when we applied our computer code to NSLS-II assuming the APS MGU to be the impedance source, we found, to our surprise, yet another possible scenario for the TMCI FB performance; we found the capacitive FB to be more effective than the resistive FB for all currents. The TMCI FB problem is now understood, and the relative effectiveness of different modes of operation can be predicted by solving appropriate dispersion relations which depend on the beam parameters and the shape of the beam impedance.

Elaboration on item (6) above:

Detailed study of the computer output for the MGU beam impedance led us to conclude that many of the low frequency resonances in the impedance are trapped TE mode resonances. Even though the TE mode does not couple directly to a highly relativistic beam, it can contribute to the beam impedance through interaction when there is a discontinuity in the beam chamber with the TM mode. We further pursue this problem in the following two ways:

(a) We built a life size model of a MGU, and excited a TE wave in a part of the MGU. Preliminary measurements indicated that the transformation from the TE wave in a part of the MGU to a TM wave in another part does occur.
(b) We built a concrete theoretical model of the mode transformation in order to gain more detailed insight into this problem. This part of the work is nearly complete.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2004	$91,415
FY 2005 (budgeted)	$140,000

Layered Cobaltates with High Thermoelectric Power

Qiang Li *04-033*

PURPOSE:

Carry out a systematic study of the fundamental thermoelectric and related material properties of layered cobaltates, necessary for their effective practical utilization. Through coordinated research on synthesis and characterization, we will be able to understand the mechanism controlling the thermoelectric properties, as well as gain the ability to tune various materials parameter in order to optimize their thermoelectric performance. The proposed research can lead to the discovery of new phenomena in strongly correlated electron systems, novel functionality, and many practical applications. This project is aligned with the BNL Grand Challenge to understand strongly correlated phenomena.

APPROACH:

Cobaltates (A_xCoO_y) are transition-metal misfit layered oxides, that features self-assembled alternatively-stacked blocks with incoherent layer boundaries, producing highly anisotropic properties along their crystallographic directions. Recently, it was discovered that some cobaltates have thermoelectric performance surpassing that of conventional thermoelectric materials. Though preliminary studies have shown that cobaltates hold great promise to be the first choice thermoelectric materials operated at high temperature and in hazardous environments, the synthesis and characterization of these materials in various forms are largely unexplored. In particular, the key issues, such as the role of self-assembly in the growth and atomic interfacial structure of cobaltates, the electronic ground state of cobaltates, and the effect of substitutions, are poorly understood. To address these key issues, we undertook a series of experimental and related theoretical investigations. We initially took a coherent, focused study of the properties and structure of $Ca_3Co_4O_9$ single crystals, and thin films grown on various single crystalline, polycrystalline, and amorphous covered substrates. A coordinated transmission electron microscope (TEM) and thermoelectric property characterization is performed to understand the growth mechanism. A theoretical investigation of Na doped cobaltates is performed in collaboration with Dr. W. Ku of the Physics Department at BNL. The density of states near the Fermi surface and quasi-particle scattering behavior are two key factors that can lead to the mechanism of high thermoelectric power. We will work closely with T. Valla and Peter Johnson of Physics Department of BNL for angle-resolved photoemission spectroscopy (ARPES) photoemission experiments. We will try to optimize the thermoelectric power through suitable substitution.

TECHNICAL PROGRESS AND RESULTS:

A post-doctoral research associate was hired in February 2004 to participate in this project. 1) We set up the three-zone furnace and successfully grew $Ca_3Co_4O_9$ single crystals, which were characterized by x-ray diffraction and magnetometer. 2) A new thermoelectric and transport characterization system was purchased from Quantum Design with BES capital funding. The system was tested and calibrated in our PPMS (properties in magnetic field) equipped with a 9 Tesla superconducting magnet. It became the main facility for

evaluating the thermoelectric properties. 3) Various thin films of $Ca_3Co_4O_9$ have been successfully grown on various substrates, including single crystalline $SrTiO_3$, $LaAlO_3$, Si, and Al_2O_3, polycrystalline Al_2O_3 using pulsed laser deposition, in collaboration with Dr. W. Si of the Physics Department at BNL. 4) High resolution transmission electron microscopy was used to characterize the microstructures of $Ca_3Co_4O_9$ films. 5) High-quality c-axis oriented $Ca_3Co_4O_9$ thin films were grown directly on Si (100) and Si (111) wafers by pulsed laser deposition without pre-chemical treatment of the substrate surface. Cross-sectional transmission electron microscopy shows excellent crystallinity of the $Ca_3Co_4O_9$ films. The Seebeck coefficient and resistivity of the $Ca_3Co_4O_9$ thin films on Si (100) substrate are 126 μV/K and 4.3 micro-Ohm.cm respectively at room temperature, comparable to the single crystal samples. This advance demonstrated the possibility of integrating the cobaltate based high thermoelectric materials with the current state-of-the-art silicon technology for thermoelectricity-on-a-chip application, such as thermochemistry-on-a-chip, bio-thermoelectric chip, and active cooling for a microelectronic processor. 6) We initiated theoretical studies of Na_xCoO_2 in collaboration with Dr. W. Ku. A sub-contract support was used for graduate Dmitri Volja focusing on theoretical modeling of Na_xCoO_2. 7) A box furnace was purchased to be used exclusively for single crystal growth of cobaltates.

In the next fiscal year, we will continue or start the following efforts: 1) We will perform detailed studies to understand the growth mechanism of $Ca_3Co_4O_9$ thin films on Si (100) and Si (111). 2) We will refine the single crystal growth with the box furnace, and measure the thermoelectric properties of refined cobaltates, single crystals and thin films. 3) We will carry out a ARPES study on the refined single crystals. 4) We will perform a series study on the substitution effect on the thermoelectric properties of cobaltates using Mg and Sr for Ca, and Cu for Co.

SPECIFIC ACCOMPLISHMENTS:

1) One peer-reviewed paper "*In situ* growth of *c*-axis oriented $Ca_3Co_4O_9$ thin films on Si (100)," Y. F. Hu, W. D. Si, E. Sutter, and Q. Li, submitted to Applied Physics Letter.

2) One invention disclose "Growth of $Ca_3CO_4O_9$ Thin Film," Y. Hu, Q. Li, and W. Si

3) Two invited presentations: (1) "Layered Cobaltates with High Thermoelectric Power," Q. Li (invited), Y. F. Hu, E. Sutter, and W. D. Si at The Direct Energy Conversion Program Review and Workshop organized by DARPA, December 13-15, 2004, Coronado, CA. (2) "Layered Cobaltates with High Thermoelectric Power," Q. Li (invited) and Y. F. Hu, at the 6th Pacific Rim Conference on Ceramic and Glass Technology, organized by the American Ceramic Society, Maui, Hawaii, September 11-16, 2005

LDRD FUNDING:

FY 2004	$ 61,780
FY 2005 (budgeted)	$101,000

Lattice QCD relevant for RHIC and AGS

Péter Petreczky *04-041*

PURPOSE:

The purpose of this LDRD project is to identify and in the long run solve lattice quantum chromo dynamics (QCD) problems. Especially those related to the Quark Gluon Plasma (QGP) created at RHIC.

APPROACH:

The theory calculations relevant to the AGS program includes the problem of hadronic contributions to the anomalous magnetic moment of the muon $g-2$ and weak matrix elements to describe rare kaon decays and determine Cabibibbo-Kobayashi-Maskawa (CKM) matrix parameters. The central question for the RHIC heavy ion program is the creation of new states of strongly interacting matter and investigation of its properties. Lattice QCD can contribute to answering these questions by first principles calculations of the relevant quantities, for example, quarkonium yield from a QGP.

Lattice QCD calculations are computationally expensive; therefore, it is difficult to control the effects of finite lattice spacing and un-physically large quark masses. The strategy to study these problems is to perform calculations in the quenched or partially quenched approximation and use chiral perturbation theory (*ChPT*) to connect to the limit of (small) physical quark masses. The following problems were addressed in FY04:

* Lattice calculations of the lowest order hadronic contribution to $g-2$ (Tom Blum)

* Problems in quenched and partially quenched ChPT in calculations of hadronic weak interaction matrix elements (J. Laiho, A. Soni)

* Lattice calculations of heavy quark potential and meson spectral functions at zero and finite temperature (T. Blum, P. Petreczky, K. Petrov, F. Zantow)

TECHNICAL PROGRESS AND RESULTS:

The lowest order hadronic contribution to $g-2$ was calculated in quenched QCD with domain wall fermions. Combined with earlier studies, these calculations show that the hadronic contribution coming from the vacuum polarization is significantly smaller than that obtained from the experimental cross-section for e^+e^- to hadrons, by about 30%. To make progress, calculations with dynamical improved staggered fermions were started and are on-going. These calculations were done in the realistic case of 2+1 flavor QCD on gauge field configurations generated by the MILC collaboration using the *asqtad* action. The (lightest) mass of the u,d quarks was ten times smaller than the strange quark mass. As the simulations were done at un-physical quark masses, chiral perturbation theory to calculate the light quark mass and q^2 dependence of the vacuum polarization was used. This allows a precise extrapolation of all of the lattice data to the physical point. Similar extrapolations, were done on the same configurations, resulting in a precise determination of f_K / f_π (total theory error of roughly 1%). A next-to-leading order chiral perturbation theory for ε'/ε was worked out. Ambiguities in quenched and partially quenched ChPT were identified. A new method to calculate the relevant low energy constants was developed.

Meson spectral functions with quark mass near the strange quark mass were studied at zero temperature in quenched and partially quenched QCD. Calculations were done using Domain Wall quarks and Wilson as well as HYP smeared Wilson quarks. Partially quenched calculations were done using gauge configurations from the MILC collaboration with improved staggered (*asqtad*) sea quarks. Lattice artifacts in meson correlation functions, which were found previously for Wilson quarks in quenched QCD, were found also in quenched calculations with domain wall quarks and Wilson quarks in partially quenched QCD. Similar lattice artifacts were found in calculations with *HYP* smeared Wilson quarks, but no exceptional configurations were found down to quark masses of about 1/8 of the strange quark masses. This means that when the high-energy limit of meson spectral functions are of interest, calculations with Wilson quarks or Domain Wall quarks may not be the most appropriate choice. For meson properties at finite temperature, *HYP* smeared Wilson quarks are a good and computationally inexpensive choice for (future) calculations with very small quark masses.

Heavy quark calculations with the so-called *Fermilab* action in quenched QCD were done. Existing codes were updated and modified to run on the QCDOC supercomputer. Calculations of meson spectral functions for the charm quark mass confirmed earlier results on survival of the J/ψ and η_c states in the plasma and dissolution of χ_c states. In addition, information about the bottomonium state χ_b was obtained.

Heavy quark potentials have been calculated in QCD with light dynamical quarks for the first time. The effect of the quark mass was studied and found to be substantial. This is a first step toward more detailed study of this quantity in full QCD on the new QCDOC supercomputer which concerns the properties of J/ψ at finite temperature in full QCD. We also extended previous calculations of heavy quark potentials in quenched QCD by calculating it at higher temperatures.

SPECIFIC ACCOMPLISHMENTS:

Results from this LDRD project were presented at two major international conferences: Lattice 2004 and Hard Probes 2004, and five papers were submitted for publication in conference proceedings. Results on hadronic contribution to $g-2$ were presented by T. Blum at Lattice 2004; results on quenched and partially quenched perturbation theory were presented by J. Laiho at Lattice 2004, where calculations of meson spectral functions at zero temperature were also presented (P. Petreczky). Finally, the results on heavy quark potential and spectral functions were presented at Hard Probes 2004 and Lattice 2004 (P. Petreczky and K. Petrov). Results on heavy quark potential in full QCD on small lattices were published in *Physical Review D*.

LDRD FUNDING:

FY 2004	$ 69,272
FY 2005 (budgeted)	$108,000

Very Long Baseline Neutrino Oscillation Experiment

Milind V. Diwan *04-043*

PURPOSE:

We propose to study in detail the physics capabilities of a very long baseline neutrino oscillation experiment based at BNL. We expect to understand how well such a facility will perform for the following goals: precise determination of the oscillation parameters Δm^2_{32} and $\sin^2(2\theta_{23})$ in ν_μ disappearance mode, detection of $\nu_\mu \rightarrow \nu$ appearance, sensitivity to $\sin^2(2\theta_{13})$, measurement of Δm^2_{21} and $\sin^2(2\theta_{12})$ in appearance mode (independent on the value of θ_{13}), verification of matter enhancement and determination of the sign of Δm^2_{32}, determination the CP-violation parameter δ_{CP} in the neutrino sector, and confirmation of CP violation by dedicated anti-ν running. We will examine the detector design to reach the required resolution and background capability. We will also optimize the neutrino beam spectrum to reach these goals. The needs of a near and far detector will be examined and a scheme to optimize the running time based on current and possible future physics understanding will be developed.

APPROACH:

Future neutrino oscillation experiments must be much more ambitious to precisely measure the parameters and, for the first time, observe violation of CP symmetry in the lepton sector. We recently studied the feasibility of a neutrino beam produced by an upgraded AGS sent over 2500 km to a massive underground detector. We concluded that such an experiment could indeed achieve the above goal. In addition, the large underground detector will be the most important facility for the study of proton decay, and atmospheric, solar and supernova neutrino physics. This bold program of experiments will put BNL and the United States in a leading position in the field of neutrino physics.

Our study is in three parts: 1) The spectrum and intensity of neutrinos from the BNL AGS accelerator: The beam-related work is in collaboration with Bill Weng and others in the Collider Accelerator Department (CAD). It includes simulations of various geometries for producing the neutrino beam. 2) The strategy for running the beam and obtaining the best possible physics result: The beam spectrum, the length of the baseline, and the capabilities of the detector are coupled in a complex way. We are attempting to understand the requirements on each so that the goals of the project can be realized, in particular the goal of measuring the CP-violation parameter. This work is carried out by both theoretical analysis (with help from Bill Marciano) and parametric simulations that attempt to approximate the detector response. 3) Simulation of detector response and detector design: Ultimately, we will need a detailed design of a large detector with mass greater than 100 kT. Brett Viren is working with colleagues from Stony Brook University (SBU) to create a simulation program while Chiaki Yanagisawa, collaborator from SBU, is using existing simulations of water Cherenkov detectors to understand the performance of such a detector.

TECHNICAL PROGRESS AND RESULTS:

We started by reviving the software written for proposal E889. Many changes were needed to make these programs suitable for the current study. We designed a new geometry for the target and horn systems to

accommodate a new, longer graphite target and to produce a more energetic beam. The spectrum that resulted from this simulation was used for the detector and physics work. Better optimization and understanding of the beam spectrum is, however, still needed.

For the physics results, initial estimates were based on analytical calculations. We performed more detailed numerical calculations by adapting old simulation codes. We parameterized the detector response using published data on water Cherenkov detectors as well as estimates produced by preliminary detector simulations. This work has formed the basis of our understanding.

We have made a list of requirements for the detector. These requirements resulted from our work on the simulations described above. Our next goal is to create a detailed detector simulation and understand the performance. We expect to work with the SBU group to create the necessary software for this purpose.

We now make some further detailed remarks about the detector simulation effort. This is carried out in collaboration with Stony Brook and Colorado State Universities (part of the Underground Nucleon Decay and Neutrino Observatory (UNO) collaboration). Work has progressed on estimating the level of rejection of backgrounds to electron appearance. Initially this is done using a large sample of Super-Kamiokande atmospheric neutrino Monte Carlo events re-weighted to the BNL flux.

The next step in this study is to develop the critical reconstruction software using UNO Monte Carlo and associated software framework. The UNO collaboration has chosen to focus on the problem of electron appearance background, and has formed a group dedicated to using UNO as a far detector for the BNL VLBL (Very Long Baseline). This group includes Brett Viren. Work on a vertex fitter, the initial step of the reconstruction chain, has finished and has shown the UNO software framework is maturing. For the time being, many of the reconstruction steps, including vertex fitting, can and will be "faked" by smearing Monte Carlo truth information with very well known reconstruction resolutions. This allows the effort to be focused on pushing the state of the art in water Cherenkov reconstruction. Such improvements will be needed to assure that electron appearance background rejection levels can be achieved. This work is very computationally intensive, but is necessary for reducing the backgrounds. To support this process both the UNO collaboration and the BNL VLBL groups will contribute processor nodes to the BNL Physics Department Cooperative Cluster, created by Brett Viren. The UNO collaboration may also build a second cluster at Colorado State University.

SPECIFIC ACCOMPLISHMENTS:

One of the laboratory reports (BNL-73210-2004-IR) is a conceptual design and a cost estimate for the 1 MW upgrade of the AGS accelerator complex and a super neutrino beam. Most of the work for this design was done by CAD personnel with extensive collaboration from us.

Another outgrowth of this LDRD is a detector R&D proposal submitted to the SBIR (DOE high-energy physics) program. We have obtained Phase II funding for this SBIR. It is listed below.

Very long baseline neutrino oscillation experiments for precise measurements of mixing parameters and CP violating effects, M. V. Diwan, et al., Physical Review D 68, 012002 (2003).

THE CASE FOR A SUPER NEUTRINO BEAM, Talk given at Heavy Quarks and Leptons 2004, San Juan, Puerto Rico, June 1 - June 5, 2004. hep-ex/0407047

THE AGS BASED SUPER NEUTRINO BEAM FACILITY (CONCEPTUAL DESIGN REPORT), W.T. Weng et al., BNL-73210-2004-IR, Oct. 1, 2004. 206 pp.

SBIR, Very Large High Gain APDs for Particle Physics, Phase II, FY2005-FY2006, PI: Mike Sivertz, April 2004, DOE high energy physics, 2 yr duration.

LDRD FUNDING:

FY 2004	$ 71,099
FY 2005 (budgeted)	$106,000

Advanced ^{3}He Detectors for the Spallation Neutron Source

Graham C. Smith *04-046*
B. Yu

PURPOSE:

The technical goal of this LDRD project is to investigate an innovative operating and readout method for ^{3}He-based neutron detectors that will permit accurate position determination in two-dimensions and large solid-angle coverage for incident fluxes higher than ever before achieved. The objective is evaluation of fundamental characteristics in a small prototype detector, from which a scaled-up instrument could be fabricated without affecting local event processing. Small-angle neutron scattering (SANS) is the primary driver for this effort, but the technique is potentially applicable to a wide range of neutron instruments.

APPROACH:

SANS instruments collect data in the direction of the incident beam, and therefore require high counting rate, two-dimensional position sensitive detectors. ^{3}He detectors have been used for most SANS machines in operation today, because of their low sensitivity to γ-rays. The counting rate of state-of-the-art ^{3}He detectors is limited to $<5\times10^5$ n s^{-1} on a 1×1 m^2 area, whereas the SNS foresees rate requirements of 10^8 s^{-1}. A promising new technical approach is a detector that operates in ionization mode, with discrete pixels, or pads, read-out in parallel. This approach has potential benefits over present ^{3}He detectors operating with some level of gas gain, particularly with respect to space-charge saturation, long-term performance ("ageing") and electronic pulse pile-up. Our group already obtained promising results from a one-dimensional system, and this LDRD will study the significantly more complex, and speculative, two-dimensional system. Charge signal profiles and amplitude distributions will be measured from an array of two-dimensional anodes pads, over a range of electric fields and electronic shaping times. This will lead to an understanding of the fundamental issues and possibly enable proof of the concepts on a prototype detector.

Collaborators are G. DeGeronimo and N. Schaknowski (BNL).

TECHNICAL PROGRESS AND RESULTS:

A test cell was fabricated from stainless-steel vacuum flanges and spacers. Inside, a 40mm deep parallel plate, ionization chamber, with negatively biased cathode (window), and hexagonal shaped anode pads at ground potential has been constructed. Figure 1 is a plan view of the anode plane. After thorough cleaning, the test cell was filled with a mixture of ^{3}He and propane: the proton/triton created by neutron conversion are stopped by the propane, and create ~ 25k electrons, which drift to the anode.

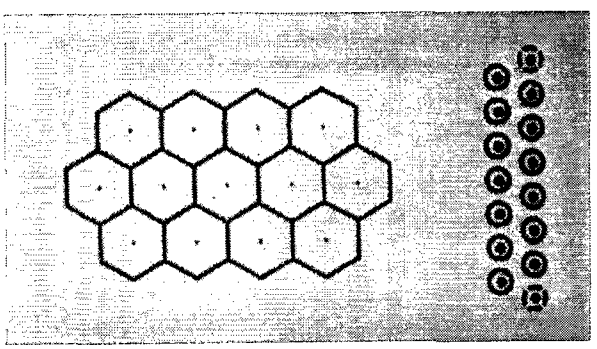

Figure 1. Anode pad board, showing 13 hexagonal pads, 5mm center to center, with printed-through holes (central to each pad) that make connection, on rear side of board, to multi-pin connection at right.

Initially, signal amplitude was measured only from the central pad of the array of thirteen, all others being directly grounded. The amplitude spectrum under uniform irradiation of neutrons is shown in figure 2.

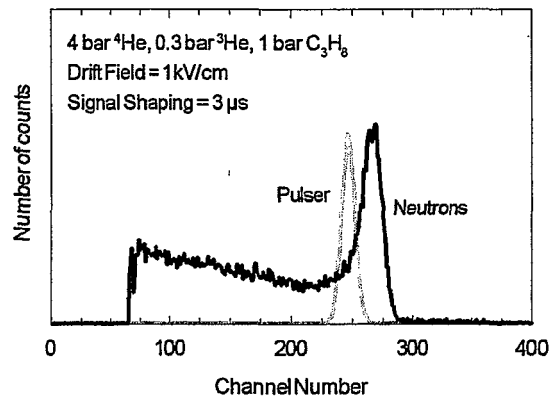

Figure 2. Pulse height distribution of charge signals from central anode pad of test cell. Black curve: uniform irradiation of neutrons, gray curve: pulser injection of 25k electrons.

This key figure confirms the basic concept that has been proposed. The neutron pulse height distribution (black curve) shows a nearly Gaussian peak, corresponding to neutron conversions in which all the electrons are collected by central pad. The signals forming the tail of smaller amplitudes are most likely from conversions in which the electron cloud has been shared between at least two pads. The percentage of events in the tail should be strongly dependent on propane pressure. Important, and encouraging, inferences from figure 2 are: i) the full-width at half-maximum (FWHM) of the neutron peak, 8%, is very narrow, ii) average total signal appears slightly greater than 25k electrons, and is well above the electronic noise level, iii) an electric field of about 1 kV/cm is sufficient to integrate virtually all of the electron charge.

Simulations with a gas depth to pad spacing ratio of 8:1 (as in this test cell) indicated that most of the electron charge should be induced in the final 10% of its drift path. This "virtual Frisch grid" operation appears validated by the well-defined Gaussian peak. Further measurements have been carried out with only 0.5 bar partial pressure of propane, to allow greater charge sharing. The pulse height distribution from a single pad contains virtually no peak. A histogram of amplitudes from any two adjacent pads (pads 1 and 2, say, figure 3) shows a significant number of neutron events in which the sum is constant (peaked ridge at 45° to axes), which correspond to sharing between pads 1 and 2 only. The plateau of lower amplitude signals, toward the origin, represents charge sharing between more than two pads. A major focus of next year's work will be evaluation of optimum propane pressure, together with determination of electron mobility for optimization of the electric field and signal shaping time.

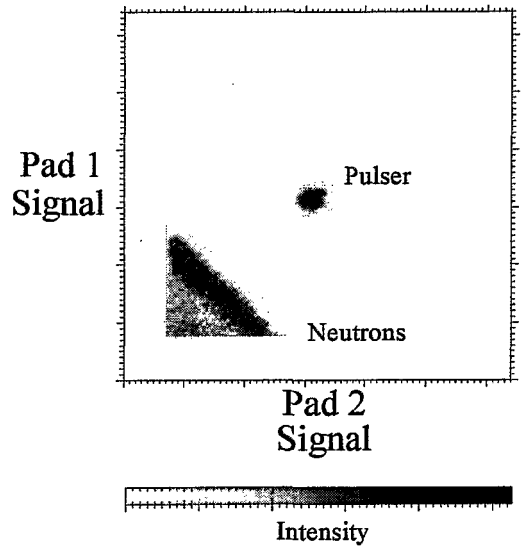

Figure 3. Two-dimensional histogram of collected charge on the central pad and any adjacent neighbor. Gas filling was 3bar ^{3}He and 0.5 bar propane, drift field: 1 kV/cm and signal shaping: 3 μs. Pulser injection is 25k electrons into each pad.

SPECIFIC ACCOMPLISHMENTS:

None

LDRD FUNDING:

FY 2004	$72,953
FY 2005 (budgeted)	$110,000

Genetic NanoTags

James F. Hainfeld *04-055*

PURPOSE:

Genomics and proteomics have advanced to where it is of interest to identify and characterize cellular complexes or "machines." In order to isolate these complexes from cells for study, genetically engineered tags have been developed to bind the desired proteins to columns for purification. Unfortunately, most larger complexes do not crystallize for x-ray studies, so these are then studied by electron microscopy. A difficulty exists in identifying component proteins (which protein is where?), and orienting smaller complexes, necessary for 3-dimensional (3-D) image reconstruction and solving the structure.

We propose to use the tags commonly genetic engineered into recombinant proteins for the purpose of biochemical purification to construct complementary gold labels that will bind to these tags. This could break the 500 kDa barrier for cryo electron microscope (cryoEM) by identifying subunits and enabling their orientation and analysis. Currently, complexes < 500 kDa are not generally solvable by cryoEM since at the low dose required, distinctive features are not perceived, and the alignment with other molecules, necessary to solve the 3-D structure, is not possible. The work we propose should make it possible for cryo-EM to solve < 500 kDa protein complexes at 10 Å resolution, which would be a significant advance for biology.

Four genetically engineered sequences were investigated and these will be programmed into and expressed in target proteins. Gold nanoparticles will be designed that will bind to these four sequences: 1) Ni-NTA-gold binding to 6x-His tags, 2) negatively charged gold to 6x Arg tags, 3) monomaleimido gold linked to cysteine, and 4) gold targeted to a gold-binding sequence.

This work will be applied to three important molecular machine complexes required for life: Ku70/Ku80/DNA-PK complex, human chromatin remodeling complex ACF, and the human ligase IV/Xrcc4 complex, all being currently worked on in the Biology Department. CryoEM single particle data will be collected in ice and reconstructions done.

This work is cogent to the DOE Genomes to Life (GTL) initiative. The first goal of GTL is: "Identify and characterize the molecular machines of life." The National Institute of Health (NIH) is investing heavily in imaging (with their new National Institute for Biomedical Imaging and Bioengineering, NIBIB) with support for cryoEM. Preliminary results from this LDRD would provide convincing evidence for follow-on funding. It would also help establish BNL as a unique cryoEM center of excellence, especially since label development is deemed highly necessary for the field. We are in a unique position to answer this need, having established both nanoparticle labeling expertise and genetic production of tagged protein complexes.

APPROACH:

Three genetically engineered sequences investigated: these will be programmed into and expressed in target proteins. Gold nanoparticles will be designed that will bind to four sequences: 1) Ni-NTA-gold binding to 6x-His tags, 2) negatively charged gold to 6x Arg tags, 3) maleimido gold to link to

cysteine residues, and 4) gold targeted to a gold-binding sequence.

This work will be applied to two important molecular machine complexes required for life: Ku70/Ku80/DNA-PK complex, and the human ligase IV/Xrcc4 complex. CryoEM single particle data will be collected in ice and computer reconstructions done to find the 3-D structures.

TECHNICAL PROGRESS AND RESULTS:

Protein production and genetic engineering: several proteins in the complexes that we are to study have now been expressed in insect cells using the bacculovirus method. This includes Ku70, Ku80, Xrcc4, ISWI, and the ACF chromatin remodeling complex. These have been engineered with the 6x-Histidine tag and for a control, without the His tag, by substituting the Flag tag. Purification of these proteins is also underway, and various columns and buffer conditions explored to maximize yield and maintain protein integrity. Under many conditions, the proteins aggregate or do not purify well. The conditions for Ku70/Ku80 and ISWI have now been worked out to reasonable satisfaction.

Gold particle synthesis: 1.8 nm gold particles with the nitrilotriacetic acid functional ligand were synthesized. These were then charged with nickel. Binding to Ku70, Ku80, and ISWI was evaluated both by blots and column chromatography. Labeling with the gold targeted to the His tag was compared to gold binding to the same proteins without the His tags. A significant problem to overcome is that we found some binding of the gold particles to proteins without the His tag, even though there was more binding to those with the His tag. Methods to eliminate this "non-specific" binding are being addressed, and include: high salt to reduce electrostatic binding, use of detergents to reduce hydrophobic interactions, and changing of the metal from nickel to copper, mercury, cobalt, zirconium, gadolinium, or europium. So far, we have not completely overcome this problem. An alternative approach is to synthesize a different ligand shell on the gold particle or to mix the NTA group with other lower binding shell ligands. We have evaluated two other ligands and demonstrated that the non-specific interactions can be completely (in one case) or almost completely overcome. However, the gold particles now have to be synthesized with some NTA functional groups included.

Electron microscopy and image analysis: Individual proteins, Ku70/80 and ISWI, and the ACF complex were prepared for negative stain EM. Ku70/80 appeared uniform, but is too small a protein complex to get much additional information by image processing. The ACF complex, although biochemically well characterized, underwent some dissociation when exposed to the lower ionic strength of uranyl acetate, which also has a pH of 3. We are now exploring chemical fixation to stabilize the complex. Image analysis software was set up and training begun of a postdoctoral student.

Some summary conclusions:

- Ku70/Ku80, ISWI, and ACF complex expressed and purified with and without the 6xHis tag.
- Gold particles synthesized with the Ni-NTA group for binding His tags
- Binding studies conducted of the gold to tagged and untagged proteins
- Electron microscopy studies to image the proteins.

SPECIFIC ACCOMPLISHMENTS :

Hainfeld, J. F., Powell, R. D., and Hacker, G. W. Nanoparticle molecular labels. *Nanobiotechnology*, C. M. Niemeyer and C. A. Mirkin, Editors, pp. 353-386, Wiley-Vch, Germany (2004).

Follow-On Funding:

"High Resolution Gold Labels for EM," National Institutes of Health 5 R01 RR017545-02, J. Hainfeld, P.I., 9/30/03 - 8/31/08, $250,000 direct for Year 2.

LDRD FUNDING:

FY 2004	$ 12,933
FY 2005 (budgeted)	$115,000

The Use of Singular Point Genome Sequence Tags to Analyze Community Composition and Metabolic Potential

Daniel van der Lelie *04-060*

PURPOSE:

This project aims at developing a high throughput approach to analyze microbial communities and their metabolic potential. The proposed technique is a unique spin-off of the Genome Sequence Tag (GST) technology that was recently developed and patented by BNL.

APPROACH:

In the original GST protocol, genome signature tags are produced at positions in the genome defined by restriction enzymes. The number of tags generated (2n) is double of the number of sites (n) for a specific restriction enzyme. In silico simulations showed that in order to analyze a 10 species microbial community, up to 1 million GST tags had to be cloned, sequenced and analyzed. To overcome this major limitation of the GST technology, a new protocol was developed based on the following considerations:

- Producing only one or a few tags per genome greatly simplifies determination of population frequencies.
- Even restriction enzymes with 8-base specificity generate ~60 tags per average bacterial genome.
- Solution: limit tag generation to a single restriction site near (but not within) a highly conserved region of microbial genomes (e.g. the 16S ribosomal RNA gene).

We used the 16S rRNA gene to develop the singular point GST technology, as it is ideal for the following reasons:

- 16S rRNA gene present in all prokaryotes.
- Database available with >60,000 16S rRNA gene entries.
- 16S rRNA copy number will define number of distinct GSTs per species.
- Tag frequencies will reflect community composition.
- Each tag will allow direct coupling with a 16S rRNA gene for species identification.

The principle of the SP-GST protocol we developed based on the 16S rRNA gene is presented in Figure 1.

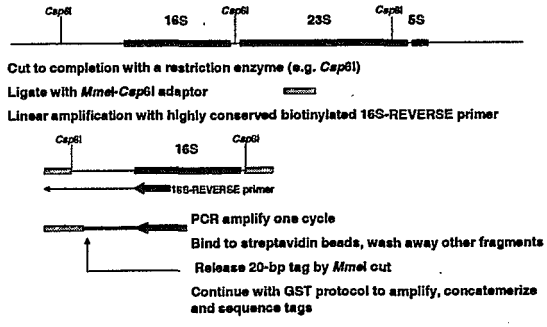

Figure 1: Principle of the singular GST technology using the 16S rRNA gene as anchor.

TECHNICAL PROGRESS AND RESULTS:

16S rRNA based SP-GST tags of pure strains. The protocol was successfully used to generate 16S rRNA gene based tags of closely related *Pseudomonas* species. The results, presented in Table 1, show that specific tags can be obtained from closely related species. The results also show that if some 16S rRNA gene containing regions have been amplified in a bacterial strain's

chromosome, the risk exists that this species will be overestimated when present in a microbial community.

- ***Pseudomonas aeruginosa***

AGCAAGCTGGTCTCCA
ATCCTTCAGGCGCTCA
GCTGTGGTTGGTGCGT
CGGCACGGCATGTCGG

- ***Pseudomonas syringae***

AGCAAGCTGGTGTCTA
CACAGCTTTGGCGGCT
GGGCGTGAATTGCCTA
ATGATGGAGAATAATC
TGGAGGAGCTTCTCGG

- ***Pseudomonas putida KT2440***

AGCGTCTGCGTGATGC
AGCAAGCTGGTGTCGA
GTTCCAGCTCCTGGTC
GGACTGATAGTCAAAA (4 times more frequent due to amplification)

Table 1: Specific GST tags obtained for closely related *Pseudomonas* species.

16S rRNA based GST tags obtained from a "simple" microbial community. A microbial community containing 4 species was used to validate the SP-GST concept and to compare it with classical molecular ecological techniques. Our comparison provided the following results and confirmed the potential of the SP-GST concept:

- 16S rDNA gene library revealed the presence of only one species.
- T-RFLP analysis gave 6 major peaks (would indicate 6 microorganisms instead of the expected 4).
- SP-GST analysis allowed the identification of 3 species.
- Quantitative PCR confirmed the presence of 3 species.

SPECIFIC ACCOMPLISHMENTS:

The SP-GST concept on the 16S rRNA gene was part of a patent application entitled "Genome Signature Tags," J. J. Dunn, D. van der Lelie, S. McCorkle, and M. Krause, Inventors, Serial Number 10/791,074, filed March 2, 2004.

Geets, J., Vangronsveld, J., Diels, L., and van der Lelie, D. The application and molecular tools to follow up bioremediation. J. Soil Sediments 3, 251 (2003).

Geets, J., Vangronsveld, J., Diels, L., Taghavi, S., and van der Lelie, D. Microbial activities, monitoring and application as part of a management strategy for heavy metal contaminated soil and groundwater. *Handbook of Remediation of Metal Contaminated Soils*, R. Naidu, N. S. Bolan, D. van der Lelie, and N. Lepp, Editors, Elsevier (submitted).

Follow-On Funding:

Composition of Microbial Communities Used for *In Situ* Radionuclide Immobilization: Natural Gene Transfer to Develop Resistance to Metal Toxicity. J. Fitts and D. van der Lelie, P.I.s, NABIR – DOE/BER, FY 2005-2007, $900,000.

LDRD FUNDING:

FY 2004	$121,236
FY 2005 (budgeted)	$188,000

3-D Electronic Wave Functions from EM Images

Joseph S. Wall 04-061
Y. Zhu

PURPOSE:

Presently available detectors in the Scanning Transmission Electron Microscope (STEM) record only a small fraction of the available information. We have designed a new detector to record over 1000 signals simultaneously, instead of the present 3. We are using image simulation to understand how to combine these signals in order to determine atom locations and charge distribution in the specimen. The TEAM Project (Transmission Electron Aberration-corrected Microscope) is a major DOE/BES effort to improve the resolution of both conventional and STEM instruments. Development of better detectors is an important aspect of our efforts, and if successful, should enhance BNL's position to obtain the second TEAM Instrument (the first is already committed to Lawrence Berkeley National Lab).

APPROACH:

STEM makes an image by scanning a finely focused probe over a thin specimen while recording the number of electrons deflected as a result of striking atoms in the object. The scan is a TV-type raster and all signals are stored and displayed digitally. The three signals recorded currently give a quantitative map of the mass distribution and this is the basis of our BNL STEM user facility with over 50 active projects.

The three signals presently used are obtained by integration over annular regions of the detector plane using scintillators and photomultipliers to give quantum detection efficiency. Large-angle and small-angle scattering detectors give dark-field images proportional to the mass of atoms in the path of the beam. These signals are useful for quantitative microscopy and imaging of atom columns in thin specimens. As valuable as this information is, it is only a small fraction of what could be used.

The actual distribution in the detector plane of the STEM consists of three components: 1) a convergent beam electron diffraction (CBED) pattern outside the disc of the transmitted beam giving information about the 3-D spatial arrangement of atoms within the probe, 2) an in-line hologram within the disc of the transmitted beam, and 3) lateral displacement of the central beam disc due to electric or magnetic fields within the area probed by the beam.

We have adapted image-simulation software to study: 1) information available, 2) detector properties needed to record it, 3) methods to extract specimen information, and 4) results to be expected on scientifically interesting specimens. The software uses the multi-slice method to accurately simulate propagation of an electron wave through a specimen containing up to 10^6 atoms, as well as the wave optics of image formation. This allows simulated imaging of all atoms in a 25 nm cube. Objects can be any known structure and can be placed on an amorphous or crystalline support and embedded in an amorphous or crystalline matrix.

In a previous LDRD, we designed a high-resistivity Si detector with 32x32 elements, high detection efficiency and high speed, suitable for STEM use. The first manifestation, fabricated in the Instrumentation Division, had a serious defect and the second is nearing completion. If successful, that detector can demonstrate the utility of the approach, which will play a

key role in future application of the TEAM instruments and strengthen BNL's case for hosting the second TEAM instrument.

To validate our approach, we have selected two specimens of interest to the NanoScience community and available at BNL: 1.4 nm diameter gold particles (catalysts) and nanotubes. Simulated data sets are being studied to determine the best method to retrieve specimen parameters. Simultaneous experimental studies will compare real and simulated measurements. In addition, we can compare to any other hypothetical or real imaging mode or instrument.

The high-risk component is the attempt to retrieve asymmetric electronic charge distributions as well as atomic coordinates for ordered and "amorphous" objects.

To aid in this project, we recruited a postdoc, Xiadong Tao. His tasks are to critique previous work in this area, work on reconstruction algorithms, and aid in data analysis.

TECHNICAL PROGRESS AND RESULTS:

This project began in February 2004. A previous LDRD lead to the design and fabrication of a STEM detector. A second version of this is nearing completion in the Instrumentation Division.

In the first nine months of this LDRD we improved the simulation program and generated simulated data for gold particles and nanotubes. This data has no practical limitations (such as vibration, finite dose, radiation damage, etc.) and is being used to test reconstruction algorithms.

Tao summarized all of the ideas regarding the "oversampling problem." Previous work by others used a parallel beam incident on the specimen. In the present work, Tao generalized the treatment to the case of a highly convergent incident beam, such as used in STEM. This will be submitted to Acta Cryst. or Ultramicroscopy after further revision.

Tao tried to retrieve the phase information from one coherent CBED pattern (nano-diffraction by Cowley) through adapting and revising a standard algorithm. However, simulation shows this method doesn't work for "unknown" crystals and amorphous materials. He found that the idea of oversampling could be used to solve the reconstruction problem for "in-line" hologram for STEM. Testing of this idea is still under way.

John Rodenburg's early research suggested that the complex potential (projection) of any object could be retrieved from collecting and analyzing a series of CBED patterns. This technique is called "Ptychography." In principle, the method can also be applied to solve this problem according to a recent paper also by Rodenburg. Tao wrote a program to test this idea. However, until now, the simulation fails. If simulation succeeds, this idea could be used for the TEAM project.

Tao also proposed to use the new CMOS detector to characterize magnetic materials. This method will be an extension of the Differential Phase Contrast Technique. Through measuring and mapping the shift of the central beam (or one reflection) through using the new CMOS detector, we can map the magnetic field in one magnetic structure. Quantitative comparison can be made between this method, other standard techniques and holography.

In FY 2005 we expect to test the version 2 STEM CBED detector in STEM3 in Biology

and produce real data for comparison to the simulations. We will investigate the effect of charged atoms and asymmetrical charge distributions in simulation and reality. We will define the extent to which we can extract 3-D atomic positions and charge distributions from data acquired with the STEM CBED detector and the increase in value of the data relative to that available with the standard integrating annular detector.

We expect these results to make a strong case for locating the second TEAM instrument in the BNL Nano Center.

SPECIFIC ACCOMPLISHMENTS:

We attended TEAM workshops and presented these ideas. We compared dark-field signals from the BNL STEM on various standard biological specimens with simulations and are preparing a manuscript describing the results.

"A simple model for diffractive imaging technique," Xiaodong Tao, Joseph S. Wall, and Yimei Zhu. Paper is in final draft, to be submitted to *Ultramicroscopy.*

An extended abstract (2 pages): "Using Iteration Algorithm to Solve the Twin Image Problem for Shadow Imaging," Xiaodong Tao, Joseph S. Wall, and Yimei Zhu, Brookhaven National Laboratory, Upton, NY, will be submitted to *Microscopy and Microanalysis 2005.*

LDRD FUNDING:

FY 2004	$ 98,945
FY 2005 (budgeted)	$150,000

Functional MRI Studies in Rats Using Implanted Brain Electrodes

Andrew Gifford *04-062*

PURPOSE:

This proposal uses the new animal MRI to perform functional MRI (fMRI) studies in rats. Our approach relies on directly stimulating neural tracts in the brain via an electrode implanted in the brain tissue. Having developed this new approach to functional brain mapping, we will address several fundamental issues that remain unclear in the neurobiology field. For example, an unresolved question is the effect of neuronal inhibition on functional brain activation. In other words, whether activity in purely inhibitory (GABAergic) brain circuits produces an increase or a decrease in regional energy demand and blood flow. Another question we will be able to answer is whether the functional connectivity of the brain reflects its neuroanatomical connectivity

The implications for success of this project in terms of BNL institutional strategy are the development and/or enlargement of a program for functional brain mapping in rodent models using MRI.

APPROACH:

To date, previous approaches to fMRI studies in rodents have almost exclusively utilized sensory stimulation to produce an fMRI signal (the BOLD response) in the sensory cortex. By directly stimulating fiber pathways in the brain using an implanted MRI-compatible electrode we can activate any region of the rodent brain, not just sensory cortex. Furthermore, we can do so under very controlled conditions, with precise control over the size and duration of the stimulation pulse. In addition to the MRI studies we confirm our findings by performing a ^{18}fluorodeoxyglucose (FDG) scan using ex vivo autoradiography.

Our approach to producing a fMRI signal in the brain is a new and untested approach. Amongst the risks are that the electrode and passage of current though it will degrade the MRI signal too much to be able to observe BOLD responses.

Dr. Congwu Du and her student have been collaborating with us on this project and have been setting up the MRI for fMRI studies.

TECHNICAL PROGRESS AND RESULTS:

Since the initiation of this project this year we have been making technical progress along four fronts: 1) development of an electrode which is non-magnetic and compatible for use in the MRI; (2) development and quantification of an electrical stimulation paradigm which leads to an effective activation of the brain areas we are targeting; (3) construction of the hardware for performing fMRI studies on rodents, namely a MRI-compatible head restraint; and (4) development of pulse sequences for performing the fMRI studies. At the time of writing we have implanted electrodes in the brains of a total of 86 rats under this protocol.

Development of a MRI-compatible electrode: After trying out many different designs we have now developed an electrode which has the desired properties of being (a) robust, (b) able to carry sufficient current to activate the brain, and (c) a low susceptibility artifact in the MRI. The electrode consists of a carbon fiber core surrounded by polyamide tubing for

insulation and rigidity. We have performed studies on both agar phantoms and in the rat to demonstrate the lack of an appreciable stimulation artifact, even when passing current through the electrode at the same intensity that produces robust brain activation.

Development of an electrical stimulation paradigm: We have conducted a large number of trials to find the optimal electrical stimulation parameters for obtaining a robust activation of fiber pathways in the brain using the implanted electrodes. Since the development of pulse sequences for obtaining a fMRI (BOLD) signal using the animal MRI are still ongoing, we performed these experiments using the approach of injecting the animal with FDG to measure regional metabolic activation using ex vivo autoradiography. From the literature it is expected that the same regions that have shown increased metabolic activation will also be those that show a BOLD response in the MRI. Using this approach, we have determined that stimulation at 100 Hz, given in 50 msec bursts @ 5/sec produces a robust brain activation. We have concentrated all our studies on mapping the brain activation from three different electrode sites, namely the motor cortex, sensory cortex and striatum. These experiments have been very successful and provided detailed maps of brain activation with which we can compare with the BOLD response from the MRI.

Construction of a MRI compatible head holder: This was completed early in the project since it is necessary for all the future studies. The head holder fits snugly in the MRI and contains ear bars and bite bars to hold the animal's head firmly in place while the imaging takes place. Imaging is performed with the animal under light anesthesia.

Development of pulse sequence for functional MRI: Although this part of the project has been moving less quickly than other aspects of the project progress is steadily being made. Dr. Congwu Du has been working to develop a pulse sequence for performing fMRI studies on the rats that can be used both by us and other users of the instrument.

Objectives for FY 2005: The primary objective will be to perform the fMRI imaging using the stimulation parameters, electrode design and target sites we have established in the project so far.

This project involves animal vertebrates.

SPECIFIC ACCOMPLISHMENTS:

Have acquired sufficient data on the pattern of brain activation from each of the three electrode sites described above to form at least one full-length manuscript, which is currently in preparation.

LDRD FUNDING:

FY 2004	$ 78,466
FY 2005 (budgeted)	$120,000

Optimizing Functional Neuroimaging Techniques to Study Brain Function in Health and Disease States

Rita Z. Goldstein *04-063*

PURPOSE:

The optimal study of functioning human brain circuits would reveal both the location and progression of the neural activities underlying mental processes. We will simultaneously combine the high spatial resolution of functional magnetic resonance imaging (fMRI) with the high temporal resolution of event-related potential (ERP) brainwave analyses. This project will bring a highly innovative technique (performed in fewer than five centers around the world) to BNL for development as a high-resolution spatiotemporal functional neuroimaging for the assessment of cognitive-behavioral (e.g., sustained attention, working memory, inhibitory control) and emotional (e.g., salience/reward attribution) brain functions. Our goal is to further the central role of the ***Brookhaven Center for Translational Neuroimaging*** as a multidisciplinary international center for neuroscience research and education.

APPROACH:

A combination of the complementary fMRI and ERP techniques is a very attractive aim in neuroscience, and a number of research groups have taken up the challenge.

Goldman et al. (*UCLA Brain Mapping Center)* developed a method for acquiring simultaneous electroencephalography (EEG) and fMRI by combining analog preprocessing and digital post-processing to strongly suppress common artifacts. Their group implemented a functional scan protocol that yields windows of artifact-free EEG between short gradient and radio frequency bursts during functional scanning.

Bonmassar et al. (*NMR Center at Massachusetts General Hospital)* recorded *sensory* ERPs using interleaved EEG and fMRI techniques. Although ERP amplitudes are much smaller than the raw EEG, their group demonstrated the feasibility of recording even small exogenous ERP components.

Kruggel et al. (*Max-Planck Institute of Cognitive Neuroscience)* has conducted combined ERP–fMRI experiments under *cognitive* stimulation using a 3 T MR scanner. Their group has studied later endogenous processes including Gestalt perception and target processing.

Other groups in the United Kingdom (Lemieux et al., *Welcome Department of Cognitive Neurology*; Allen et al., *National Hospital for Neurology and Neurosurgery*) reported on the basic science and clinical utility of the EEG/fMRI combination for localization of the generators of interictal epileptiform discharges.

Our laboratory has developed a response inhibition paradigm for examining reward processing and motivation in both fMRI and ERP environments. We have recorded control subjects as they performed the task during separate fMRI and ERP sessions. Amplitudes of the cognitive P300 ERP component were significantly larger in monetarily motivating conditions, and corresponded with subjective ratings of interest and excitement about the task. During fMRI in normals and cocaine addicts the task produced a distinct pattern of activation in the orbitofrontal cortex of cocaine addicts that mirrored subjective reports showing deficits in reward processing. We expect to find similar reward processing deficits in cocaine addicts under our ERP paradigm, as reflected by P300 amplitude and self-report measures.

TECHNICAL PROGRESS AND RESULTS:

During 2004, the hardware and software components required to acquire and analyze human cognitive ERPs were identified and acquired. After consideration of several state of the art alternatives - which included extended discussions, site visits to the fMRI centers at Yale University and Massachusetts General Hospital and an invited presentation by Giorgio Bonmasser here at BNL - a leading commercial ERP system from NeuroScan was ultimately selected and has recently (11/04) been delivered. Modifications of the existing research protocol (#328) to incorporate ERP testing were completed and have been approved by the BNL Institutional Review Board. During FY04-05 twenty cocaine addicted subjects and 20 healthy controls will be scheduled for ERP studies.

Acquisition of fMRI compatible hardware to enable ERP recordings in the magnetic environment will occur during 2005. The NeuroScan system is now being installed for independent use outside the fMRI environment to begin operator training and the development of cognitive tasks that will be used during simultaneous fMRI/ERP recordings planned for 2005.

This project involves human subjects.

SPECIFIC ACCOMPLISHMENTS:

1. **Goldstein** RZ, Volkow ND, Tomasi D, Caparelli EC, Berry SA, Leskovjan AC, Telang F, Chang L, Ernst T. A modified role for the orbitofrontal cortex in attribution of salience to monetary reward in cocaine addiction: an fMRI Study at 4 T. Human Brain Mapping Annual Meeting, Budapest, Hungary, June 14, 2004.
2. **Goldstein** RZ, Leskovjan AC, Hoff AL, Hitzemann R, Bashan F, Khalsa SS, Wang GJ, Fowler JS, Volkow ND. Severity of neuropsychological impairment in cocaine addiction: association with metabolism in the brain reward circuit. College on Problems of Drug Dependence, Puerto Rico, June 12-17, 2004.
3. Alia-Klein N, O'Rourke T, **Goldstein** RZ, Cottone LA, Volkow ND. Cannabis interacts with specific psychotic symptoms to increase severity of violent behavior in individuals with psychotic disorders. College on Problems of Drug Dependence, Puerto Rico, June 12-17, 2004.
4. **Goldstein** RZ, Tomasi D, Cottone LA, Telang F, Caparelli EC, Zhang L, Leskovjan AC, Chang L, Ernst T, and Volkow ND. Loss of sensitivity in appraising relative saliency of money in drug abusers is associated with disrupted activity in orbitofrontal cortex. Society for Neuroscience, San Diego, October 2004.
5. **Goldstein** RZ. Neuroimaging evidence for a modified function of the orbitofrontal cortex in human cocaine addiction: implications for stress induced relapse. Symposium on "Stress and relapse in drug addiction: lessons from human neuroscience," the Society of Biological Psychiatry annual meeting, New York, NY, May 1, 2004.
6. **Goldstein** RZ, Cottone LA, Alia-Klein N, Leskovjan AC, Fowler JS, Wang GJ, Gur RC, Hitzemann R, Volkow ND. The neurobiology of anger in cocaine addiction: role of the lateral orbitofrontal gyrus. College on Problems of Drug Dependence, Puerto Rico, June 16, 2004.
7. Alia-Klein N, **Goldstein** RZ, Tomasi D, Cottone LA, Wang G-J, Fowler JS, and Volkow ND. The word "NO" activates areas associated with negative emotion and inhibitory control. Society for Neuroscience, San Diego, October 2004.

LDRD FUNDING:

FY 2004	$100,684
FY 2005 (budgeted)	$150,000

Technological Development of a Fluorescence Probe for Optical Detection of Brain Functional Activation *in vivo*

Congwu Du *04-066*
H. Benveniste

PURPOSE:

The objective of this project is to develop an optical probe that concurrently tracks blood volume, tissue oxygenation and intracellular calcium changes in the rodent brain *in vivo*. The new optical probe will provide new modalities for future brain functional studies by measuring calcium transients from a brain surface, and will compliment other strategic and planned 'Life and Physical Science interface' initiatives in drug addiction and developmental research at BNL.

APPROACH:

In spite of our previous success with calcium fluorescence studies in the whole perfused heart using the calcium indicator Rhod2, it is clearly a technical challenge to integrate multi-instrumentation functions such as blood volume, oxygenation and calcium into a single probe design. The difficulties are primarily due to tissue absorption, scattering and physiological interferences caused by the variation in blood volume and oxygenation in the tissue. Such interferences impose obstacles to detection of calcium transients at the cellular level (i.e., $Ca^{2+}{}_i$) because they interfere with signal-to-noise ratios and sensitivity when the calcium indicator binds to calcium. One of the initial goals was to design a prototype photo-spectrometer suitable to trace changes in intracellular calcium along with the changes in blood volume and tissue oxygenation, and examine the detection sensitivity and instrumental feasibility by means of phantom and animal studies.

Milestones for FY 2004 were 1). developing a prototype photospectrometer with multiple-modalities to measure the changes in blood volume and tissue oxygenation as well as intracellular calcium; 2). characterizing the loading parameters of the calcium indicator Rhod2 for calcium labeling in tissue phantoms; 3). examining the sensitivity of calcium dependent fluorescence detection *in vivo*.

TECHNICAL PROGRESS AND RESULTS:

A prototype photospectrometer was developed. It consists of a 150-W Xenon lamp; a fast excitation monochromater (Mono-Ex) synchronized with a shutter in the fluorescence channel to control the band pass filter on and off, and the photon-counting detectors for fluorescence (PMT-F) and diffuse reflectance (PMT-A). The lamp is connected to a computer-controlled monochromater to select the incident wave-lengths of 548nm, 555nm and 572nm by time-sharing to sequentially deliver these onto the brain surface through one arm of a Y-shape bifurcated fiber-optic bundle. These wavelengths were purposely selected to sensitize the expected signals. The fluorescence and the diffuse reflection re-emitted from the brain are collected by the fiber optic tip of the common leg and transferred through the outgoing leg of the bundle. After passing through a beam splitter, 5% of the signal intensity is reflected for diffusion photon detection by PMT-A, whereas 95% is delivered to PMT-F for fluorescence detection. A band-pass filter centralized at 589nm with 10 nm band-width was placed in font of the PMT-F to purify the fluorescence emission at 589nm. A shutter in front of PMT-F is synchronized with the monochromater to pass the fluorescence emission through while

exciting at 548nm and blocking the incident light at 555nm and 572nm reflected to PMT-F. The diffusive re-emissions at 548nm, 555nm and 572nm from the brain tissue are detected by PMT-A. The signals are digitized and stored in a personal computer for data processing.

Tissue phantom studies were performed to predefine the loading parameters for calcium labeling using calcium indicator Rhod2. Our experimental results demonstrated that 1) Rhod2 distributes in a perimeter around the injection tip, and the 50% value of the maximal intensity is ~4 mm away from the injection center at an given flow rate; 2) the infusion rate impacts the intensity of Rhod2-Ca_i^{2+} fluorescence emission, that is, the higher the infusion rate the more loading of Rhod2 and the better the signal-to-noise ratio. 3) the oblique injection (i.e., microinjection with an angle of ~30°—45°) can be used to improve the Rhod2 distributing homogeneity in certain layers. These phantom studies helped to predefine the loading Rhod2 parameters for labeling calcium in the brain, i.e., a microinjection with a 3μl/min perfusion rate under an oblique delivery configuration was adapted for these studies.

Animal study was initiated to examine sensitivity for calcium-dependent fluorescence detection from the living brain in vivo. The experiments were performed in the brain of rats using a transient cerebral ischemia model. Based on our pervious finding, the cerebral ischemia induces an excessive increase of intracellular calcium. The model is reversible upon restoration of circulation, which can be used to test the instrument's ability to detect calcium changes in highly scattering tissue such as the brain. Our primary results indicate that the calcium-dependent fluorescence intensity changed during ischemia and reperfusion, thus demonstrating the feasibility of detecting intracellular calcium signal from the surface of living brain.

SPECIFIC ACCOMPLISHMENTS:

Publications:

"Simultaneous detection in vivo of changes in cerebral blood volume, oxygenation and intracellular calcium during cerebral ischmia and reperfusion using photospectrometry," *Du C.*, Koretsky A. P., Igore Izrailtyan, *Benveniste H.*, *J. of Cerebral Blood Flow & Metabolism*, 2004 (in revision).

Abstracts and Presentations:

1. Du C., Koretsky A. P., Benveniste H., "Simultaneous measurement of blood volume, oxygenation and intracellular calcium in the rat brain in vivo," Gordon Research Conference on Brain Energy Metabolism and Blood Flow, August 8-13, Waterville, Maine, 2004.

2. Wolf A., *Du C.*, Pan Y., Benveniste H., "Imaging rat brain function using calcium-sensitive fluorescent dye Rhod2," Biomedical Engineering Society Annual Meeting, Oct 13-17, Philadelphia, 2004.

3. Du C., Izrailtyan I., Benveniste H., "A new fluorometric and optical technological approach for tracking of intracellular calcium, blood volume and oxygenation changes in the rat brain in vivo," Optical Society America Biomedical Topical Meeting, April. 14-17, Florida, 2004.

4. Du C., "An optical probe for a simultaneous detection of blood volume, oxygenation and intracellular calcium from rat brain in vivo," invited talk in Johnson Foundation (Dr. Britton Chance's Laboratory), Univ. of Pennsylvania, Philadelphia, PA, April 2004.

5. Du C., Izrailtyan I., Benveniste H., "Optical and fluorescent imaging in vivo at BNL," NIBIB-DOE Workshop on Biomedical Imaging: Optical and X-ray Technologies, Feb. 10-11, Maryland, 2004.

6. Du C., Izrailtyan I., Benveniste H., "Fluorescence and optical detection of brain activation in vivo," DOE Workshop on Neuroimaging. Oct. 27-29, Massachusetts, 2003.

Internal Report:

"A New Fluorescence and Optical Imaging Method to Visualize Ischemia-induced

Intracellular Calcium Changes During L-channel Calcium Blockade," Yinette Perez, (summer student from CCI program), Congwu Du and Helene Benveniste, reported to DOE, August 2004.

Grant Proposal Funded:
"A Multi-modality Optical Instrument for Functional Activity Studies in the Living Rat Brain," FWP grant 'Novel Phenotyping by multi-modality imaging' $650,000/yr, sub-project IIIb. PIs:Congwu Du and Helene Benveniste. October 2004 - 2009.

LDRD FUNDING:

FY 2004	$ 27,032
FY 2005 (budgeted)	$130,000

Nuclear Control Room Unfiltered Air In-Leakage by Atmospheric Tracer Depletion (ATD)

Russell N. Dietz *04-069*

PURPOSE:

Nuclear plants with a licensing based, in part, on low control room (CR) unfiltered air in-leakage (UI) rates (<50 cfm), need to use a tracer approach that directly measures this value; the standard tracer approach, which determines this value by difference, can result in an unacceptably large uncertainty. The goal is to use the ATD approach at actual low in-leakage nuclear plants as the method for generating mandated results, which will be reported to the NRC (Nuclear Regulatory Commission). New programs supported by specific nuclear plants for generating these NRC-required results will be a measure of the success of this project. There is a further mandate that such UI determinations be repeated on a tri-annual basis; once applied to a particular plant, repeat testing could be conducted less expensively by utility personnel employing ATD with Brookhaven only performing the state-of-the-art analyses. Improved analyses will also benefit new homeland security and CO_2 sequestration tracer projects.

APPROACH:

Background. The mathematical hypothesis of this project was that the efficient removal of the ambient background concentration of certain perfluorocarbon tracers (PFTs) by the plant's installed charcoal systems provides the means for the direct determination of UI. At steady state (SS), CR concentrations equal to those out of the charcoal implies no UI; a slight increase in the CR concentration means a slight amount of UI. The CR concentration relative to that in normal ambient air times the rate of charcoal-filtered air provides the UI quantification. This ATD approach has not been previously applied. The exploratory issues pertain to an assessment of the likely performance of installed charcoal systems for the nearly 100% removal of certain PFTs and the development of the sampling and analysis strategies for the successful quantification of the expected few one thousandths of the normal 5 to 10 parts per quadrillion ambient concentrations; this will be a significant extension of the PFT technology.

Scope. **1)** Testing of commercial-grade nuclear charcoals for nearly 100% removal of PFT was a primary requirement and an essential task. An ASTM-type test cell and sampling apparatus is being used. **2)** Tent-testing of charcoal filtration systems at an actual nuclear plant with intentional release of tracer will be used to compare the UI results had the testing been done by ATD alone. **3)** Accelerated depletion of PFT backgrounds in a large-volume CR to advance time to SS required the evaluation of commercial portable charcoal-filtration units for PFT removal efficiency. **4)** The resulting low (~10^{-3} of ambient) concentrations required the application of higher sampling rate systems and demonstration of their efficiency. **5)** Analyses of these very low concentrations and the presence of other organic constituents emitted from the clean-up charcoal required studies on the gas chromatograph system normally used only for clean ambient air analyses (GC2). **6)** ATD testing will be done at a commercial nuclear plant. **7)** Repeat-testing techniques will be developed so plant personnel can handle the field effort – at reduced costs.

Methods. Standard laboratory procedures are being used to conduct this research – with the exception of the state-of-the-art GC2 system and the use of nuclear control room facilities for conducting final demonstrations of ATD.

TECHNICAL PROGRESS AND RESULTS:

This project started in February 2004. FY 2004 results included: **1)** Testing of the first charcoal type under several conditions showed PFT removal efficiencies adequate for ATD to work

– 99.90 to 99.94%. **2)** Four installed charcoal systems at an actual nuclear plant were tested for UI by our conventional PFT approach. This project allowed the examination of additional sampling done to place an upper bound on those rates with the ATD approach:

Four Charcoal Systems' UI, cfm

System	Tent Test	ATD Bound
MCR U1	15.6 ± 3.2	<17.8 ± 0.3
MCR U2	13.3 ± 0.5	<15.8 ± 1.2
SWGR1	8.5 ± 0.4	<11.5 ± 1.1
SWGR2	26.8 ± 2.0	<38

It was clear that ATD should work – as long as we measure the PFT concentration in the discharge of the charcoal. **3)** Commercially-available temporary portable charcoal 1000-cfm systems were evaluated at 2 other nuclear plants; they had good efficiencies and were able to deplete PFT concentrations to SS in a few hours. **4)** Two high flow rate systems were implemented – 9 sequential air samplers (SASs) built in the mid 80's were refurbished and 4 Air-Pro (AP) dual-channel flow-controlled pumping systems were used to quantitatively collect 30 to 150 L air samples at 30 L/h; back-up sampling tubes (CATS) on the APs showed good efficiency with negligible break through – even when sampling on charcoal system exhausts (high levels of organic vapors can cause loss of CATS sampler efficiency). **5)** Analyses of actual nuclear plant samples showed quantification difficulties with critical PFT peaks; some use of heart-cutting (throwing away certain peaks) improved results. **6)** The first ATD testing, where the utility is relying solely on this technique, was conducted at two nuclear plants, one in August and the second in Sept 2004. The goal of quantifying low UI rates was achieved; rates of 5 to 10 cfm were quantified with 10 to 20% uncertainty. The ATD approach will likely replace conventional tracer testing over the next year or two as the results become more widely disseminated.

The testing of a variety of charcoals must be done as well as examining why certain installed systems have less than the expected efficiency; this will require the cooperation of nuclear plants to obtain samples of in-place charcoal. Further evaluation of the efficiency of the CATS samplers at the high flow rates in the presence of organic vapors from charcoals must be conducted. Some evidence indicates that installed systems could be leaking; field data will be reviewed to see if ATD can quantify this. Further optimization of the heart-cutting capability will be used to improve analyses on these low-level samples. Results from the first two nuclear plants using ATD only will be sent to the NRC by about April 2005; it is planned to present these results to the nuclear utility industry some time in July 2005. Repeat-testing procedures and tools will be established.

SPECIFIC ACCOMPLISHMENTS:

The most significant accomplishment has been the acceptance of the ATD approach by the two nuclear plants with their concomitant funding of $350K to provide testing and results to be submitted to the NRC. The reports of their results have been presented to each of those utilities and will be presented in a more-public forum in mid 2005.

A patent application was submitted but the ATD approach was deemed not to be patent-able.
A paper on the development of this approach and the laboratory testing results will be prepared in FY 2005.

Funding of other nuclear plant tests of UI are expected to arise once the results from the two plants recently tested are accepted by the NRC.

LDRD FUNDING:

FY 2004	$59,463
FY 2005 (budgeted)	$90,000

Perfluorocarbon Tracer Sampling, Tagging and Monitoring Techniques for use at the Urban Atmospheric Observatory

John Heiser *04-073*

PURPOSE:

This program is designed to study the transport and spread of weapons of mass destruction, chemical, biological, radiological or nuclear (WMD/CBRN) materials in the event of a terrorist attack has been initiated. The primary objective is to enhance NYC's emergency capabilities for responding to potential airborne releases of harmful contaminants. An essential component of Urban Development Program (UDP) is conducting field studies in NYC to provide data for improving and validating atmospheric models to simulate contaminate dispersal.

Perfluorocarbon tracers (PFTs) are uniquely qualified to provide the data necessary for urban atmospheric model validation. PFTs can be used to safely simulate behavior of contaminants under actual conditions within urban environments where it is particularly difficult to accurately predict fate and transport. This project is developing the crucial engineering hardware, methodology and software required to fully exploit the capabilities of perfluorocarbon tracers (PFT) to study transport of airborne contaminants in an urban environment with specific emphasis on the difficult topography presented by the deep urban canyons unique to NYC (average building height in the test area is 40 meters).

APPROACH:

The BNL Tracer Technology Center, headed by Russell Deitz, is uniquely qualified to perform atmospheric PFT studies. The Center's scientists, engineers and technical collaborators have done pioneering work in the development and practical use of perfluorocarbon. This expertise will be used to develop the equipment, methods and protocols for PFT sampling in the deep urban canyon.

To this end, an initial UDP tracer and meteorological field study is planned for an area surrounding Madison Square Garden (MSG; W 33rd Street and 8th Avenue in Midtown Manhattan). Very small amounts of safe, inert PFTs will be released, outdoors, at ground level near MSG. Tracer sampling and meteorological measurements will be made in an area within approximately ¼ mile radius of MSG. Two days of tracer studies will be accomplished during a two-week period. The two-week period is intended to allow for at least two days of settled weather for conducting the tracer releases.

Six PFTs will be released near MSG from five locations (for QA/QC, two at one location). Dispersion of the tracers will be determined by collecting air samples at various locations. The samplers are portable, battery-powered units that will be attached to light poles at about three-meters above ground at each of 21 locations extending out to 400 meters from MSG (total of 21 samplers). To determine the vertical extent of the tracer plume, ten portable tracer samplers will be placed at five locations on surrounding buildings (One Penn Plaza is proposed to have eight samplers at four locations, and Two Penn Plaza is proposed to have two samplers at building-top). Two portable tracer samplers are proposed to be located in Penn Station to give an indication

of the infiltration of tracers into Penn Station. Tracer samples will also be collected using personal tracer samplers that will be carried by 12 individuals located in and around the MSG area and Penn Station. Each individual will have a fixed location or predetermined path to travel during the two tracer sampling days.

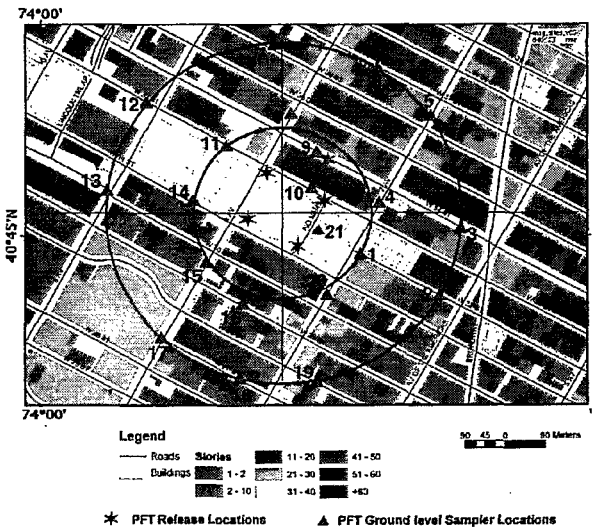

Figure 1. Ground level Air Sampling Locations for MSG Field Study

Figure 2. Vertical Air Sampling Locations for MSG Field Study

TECHNICAL PROGRESS AND RESULTS:

Current Brookhaven Atmospheric Tracer samplers (BATS) are over 25 years old and prone to failure. While the lids, containing the collection tubes are still "state-of-the-art," the operational bases are long past their prime and no where close to state of the art. This project is developing a new version BATS base that will allow digital programming (old versions were manually encoded), have Wi-Fi capabilities to allow on-the-fly changes and will have variable and changeable on-the-fly sample intervals, pump rates and start/stop times. During FY 2004 we developed a prototype of the next generation air sampler. This unit operated off a PDA (personal digital assistant) which has Wi-Fi built in.

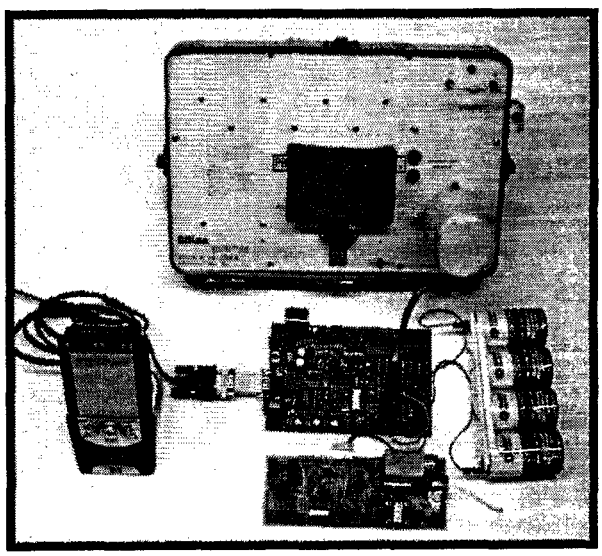

Figure 3. Prototype of air sampler

The PDA was programmed using Embedded Visual C++ to have the functionality of the BATS logic through a graphical user interface. To activate the pump and valve assembly, the PDA was connected to a simple circuit board through a nine-pin serial cable. This circuit board was developed with a PIC18F1320 microcontroller to read serial input signals and provide motor controllers to activate the

pump and valves on the BATS lid. The benefits of using a PDA are its programmability and it's ability to change sample periods on the fly using 802.11b wireless internet. Although this solution still requires circuitry, it was simple and inexpensive to develop a working prototype. The circuitry needed was uncomplicated because all of the behavior of the unit was stored in memory on the PDA.

John Nagy and Raymond Edwards of the BNL Earth Systems Science Division will be collaborating on the final prototype which will include a new pumping system with variable, controlled air flow, low power characteristics and Wi-Fi file exchange. This unit may also replace the unit PDA with a single rugged chip with the program interface being web based through a central computer or PDA.

The fieldwork plan for the planned MSG study was completed. A series of workshops took place under the UDP banner. The experts gathered at these workshops to help formulate the work plan. We have received DHS approval of the plan and are now working on final NYC OEM approvals. The interest generated in this project has led to DTRA (Defense Threat Reduction Agency), DHS (Department of Homeland Security) and EPA (Environmental Protection Agency) all joining in the MSG study as well as adding funding. The MGS study is expected to take place in March or April of 2005.

SPECIFIC ACCOMPLISHMENTS:

Field Work Plan, New York City – Urban Dispersion Program, Madison Square Garden Field Study – December 2004, Compiled by Jerry Allwine (Pacific Northwest National Laboratory), Field Team Leads and Contributors: John Heiser, Michael Reynolds, and Paul Kalb (Brookhaven National Laboratory); Jerry Blancato and James Deloia (U.S. Environmental Protection Agency), Paul Lioy (Rutgers Environmental and Occupational Health Sciences Institute), and Steve Hanna (Harvard School of Public Health).

PLANS FOR THE MADISON SQUARE GARDEN 2004 (MSG04) TRACER EXPERIMENT IN MANHATTAN, Steven Hanna, Michael Reynolds, John Heiser, and Robert Bornstein, Fifth Conference on Urban Environment, American Meteorological Society, Vancouver, BC, Canada, August 2004.
[http://ams.confex.com/ams/pdfpapers/80756.pdf]

LDRD FUNDING:

FY 2004	$ 65,530
FY 2005 (budgeted)	$100,000

Development of an Aerosol Mobility Size Spectrometer and an Aerosol Hygroscopicity Spectrometer

Jian Wang *04-079*

PURPOSE:

The technical objective of this project is to develop two novel instruments. The first instrument, referred to as the Aerosol Mobility Size Spectrometer (AMSS), will be capable of measuring aerosol size distributions for the entire diameter range of 15 nm to 1000 nm within ~1 second. AMSS offers a factor of 50 improvements in time resolution over current state-of-the-art research instruments. The second proposed system, referred to as the Aerosol Hygroscopicity and Volatility Spectrometer (AHVS), will be capable of measuring size-resolved aerosol hygroscopicity and volatility over the diameter range 15 nm to 600 nm within ~2 minutes. Both instruments will significantly improve our ability to characterize atmospheric aerosol properties and to study the evolution of aerosols (e.g. size distribution, hygroscopicity, and chemical composition) as they are transported downwind of their sources.

APPROACH:

The current incomplete understanding of atmospheric aerosol properties and their controlling processes necessitates further intensive field projects involving aircraft-based measurements. As a result of slow measurement speed of current techniques, accurate measurements of aerosols with high spatial variation, such as aerosols in the vicinity of clouds or inside a pollution plume, are not possible onboard research aircraft. The proposed AMSS addresses the issue of measurement speed by measuring charged particles of different sizes simultaneously. Figure 1 shows the schematic of the proposed AMSS, which consists of five major sections. Figure 1(a) and 1(b) give the side and front views of the AMSS, respectively. Aerosol samples are first charged in an aerosol charger. The charged aerosol particles are then introduced into the separation chamber through a narrow slit. A constant electric field perpendicular to the flow direction is established inside the separation chamber by applying a high voltage to one side of the chamber and grounding the other side. Under the influence of this electric field, charged particles are separated into different flow streams/locations according to their mobilities (sizes). The separated aerosol particles then enter a saturator, in which there is no applied electric field, and the sample flow becomes saturated with organic vapor. The subsequent cooling of the sample inside the condenser generates a high supersaturation that activates particles as small as 15 nm in diameter. After aerosol particles grow into supermicron droplets, they are detected by an imaging system. A laser beam is collimated into a sheet of light, which illuminates the particles as they cross. The images of particles are recorded by a high speed CCD camera. Recorded particle images provide both the size dependent position (in the *y*-direction, figure 1c) and the concentration of particles, which are then used to derive aerosol size distributions.

Dr. Pramod Kulkarni and Dr. Peter Takacs participated in this project.

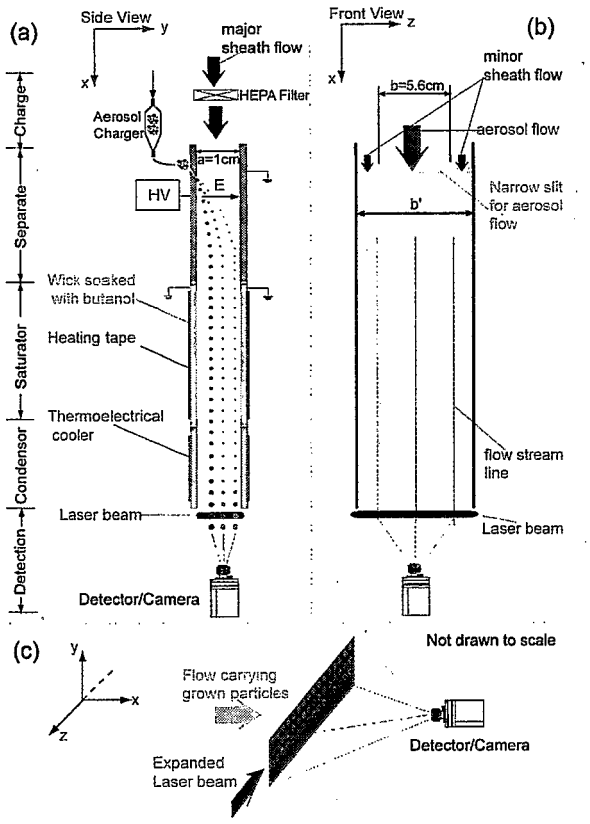

Figure 1. Schematic of the Aerosol Mobility Size Spectrometer (AMSS).

TECHNICAL PROGRESS AND RESULTS:

Detailed theoretical analyses and numerical simulations were performed for the AMSS. The theoretical analyses included the measurement range and the size resolution of the proposed AMSS. The flow field, particle trajectories, and particle activations inside the AMSS were simulated using finite element modeling software (FEMLAB). The effects of Brownian diffusion and temperature gradient on the accuracy of size measurements were studied through detailed simulations of particle trajectories inside the AMSS. We also examined the edge effect of the electrical field on particle size measurements. Based on the analyses and simulations, we have determined dimensions and operational parameters of the AMSS. The development of a prototype instrument has started. The main body of the prototype instrument has been constructed, and we have successfully implemented flow and temperature control of the prototype instrument. A preliminary design of the AMSS imaging system has been completed and evaluated using optical design software (ZMAX), and the laboratory test of the imaging system is underway.

In FY 2005, we will finish the testing of the imaging system and the development of the prototype AMSS. The performance of the prototype AMSS, including the measurement speed, size resolution, and the size range, will be characterized and studied in the laboratory.

SPECIFIC ACCOMPLISHMENTS:

The concept and design of the AMSS were presented by P. Kulkarni and J. Wang at the annual conference of the American Association of Aerosol Research, held in Atlanta, GA, Oct. 4-8, 2004.

An invention disclosure has been submitted to the Laboratory's Office of Intellectual Property and Sponsored Research for the AMSS. We also received funding for deployment of AMSS during future field projects from the Department of Energy Office of Science through Atmospheric Science Program: $253K for FY 05, $262K for FY 06, and $269K for FY07.

LDRD FUNDING:

FY 2004	$65,589
FY 2005 (budgeted)	$100,000

Exploration of Thermal Diffusion Processes in CdZnTe for Improved Nuclear Radiation Detectors

Aleksey Bolotnikov *04-086*

PURPOSE:

The goal of the project is to achieve adequate detection efficiency and high spectral resolution of CdZnTe (CZT) detectors by extending the uniform electric field throughout the full volume of the collection region of CZT devices.

APPROACH:

We propose to employ a PIN junction structure for CZT devices that are similar to structures developed for Ge and Si detectors. Two approaches are to be tested to achieve the goal: (1) by making Schottky barrier contacts, and (2) by thermal diffusion of p-type dopants at high temperatures >500 C. The later approach leads to the formation of PIN junctions near the contacts which is equivalent to the first approach, but it provides a more reliable and controllable way of fabrication of blocking contacts on CZT surface.

The use of the PIN junction is known to be the best approach to achieve full depletion of the active volume of the semiconductor detectors with minimum leakage current.

The objective is to measure the changes in leakage current and CZT device response to gamma radiation.

TECHNICAL PROGRESS AND RESULTS:

During FY 2004, we investigated the first approach by showing an improvement in the spectroscopic properties of PIN junction CZT detectors. We fabricated several devices with virtual Frisch-grids (bar detectors). Such contact configuration gives us the opportunity to study improvements in both the uniformity of the electric field and spectral resolution. We developed the pulse shape analyses and x-ray scan system to canalize the lateral and depth uniformity of the electric field inside the bar detectors. We developed and characterized a process of making high-quality Schottky contacts on CZT samples which provide full depletion of the bar detectors at relatively low leakage currents. We developed and characterized a special chemical treatment of the CZT side surfaces. With long (> 10 mm) CZT devices we achieved an energy resolution 1.3% and 1.2% at 662 keV for the devices fabricated of CZT material grown by high-pressure and low-pressure Bridgman methods. We achieved high uniformity of the device responses, verified with both the x-scans and waveform technique, which indicates the full depletion of the CZT crystals.

We investigated the possibility to thermally diffuse p-type dopants at > 500 C. This is a very complex procedure that requires fulfillment of many safety precautions and careful planning. Unlike Si and Ge semiconductors, CZT cannot withstand high temperatures. The Te (and dopant) vapor pressure growing with increasing temperature, raised many environmental and safety issuers which made it very difficult for the actual realization of the thermal diffusion process. Furthermore, from analyses of the literature and based on our preliminary measurements, we found that the HPB grown CZT material might irreversibly lose its semi-insulating property already above 150 C. The heat process used for thermal diffusion disturbed the compensation mechanism responsible for high resistivity and electron lifetime CZT. The annealing must either change the energy

location or level in the bandgap of the compensation dopant impurity. So currently we consider the first approach to be more reliable and practical for the utilization of CZT material.

In FY 2005 we will continue to pursue our goal to employ high-temperature thermal diffusion. However, as a first step, we will study the effects of the low-temperature (< 150 C) annealing process on the Schottky contacts and the performance of detectors made of CZT crystals grown by different techniques. This will justify the thermal diffusion process. We will also investigate other factors affecting the depletion of CZT devices and their performance.

SPECIFIC ACCOMPLISHMENTS:

A. E. Bolotnikov, G. S. Camarda, G. A. Carini, G. W. Wright, R. B. James, D.S. McGregor, W. McNeil, "New Results from Performance Studies of Frisch-Grid CdZnTe Detectors," SPIE, 5540, pp. 33-45, 2004.

A. E. Bolotnikov, G. C. Camarda, G. A. Carini, M. Fiederle, L. Li, D. S. McGregor, W. McNeil, G. W. Wright, and R. B. James, *Fellow, IEEE,* "Performance Characteristics of Frisch-Grid CdZnTe Detectors," to be published in IEEE, 2004.

LDRD FUNDING:

FY 2004	$86,077
FY 2005 (budgeted)	$130,000

An Integrated Approach of High Power Target Concept Validation for Accelerator Driven Systems

Nicholas Simos *04-088*

PURPOSE:

The success of a number of proposed high power accelerators is strongly linked to the ability of a few, non-conventional materials and composites to withstand high levels of irradiation damage combined with severe shock from intercepting energetic protons. The objective of this project is to explore, through a systematic and detailed experimental effort, the feasibility of a number of innovative new materials as accelerator production targets. Specifically, assessment of the irradiation effects on key physical and mechanical properties, which make these materials attractive in the first place, is sought through controlled irradiation exposure and post-irradiation tests.

Proof of irradiation and shock resilience of these novel materials will form the basis for BNL program development related to:

- Accelerator initiatives such as the Muon Collider, the Neutrino Superbeam, the Next Linear Collider, etc.
- NASA's search for multifunctional materials performing shielding and structural functions while maintaining properties under irradiation exposure.
- Special industrial applications of these materials, including material surface treatment (irradiation effects on nano-film deposition, and plating).

APPROACH:

The challenge, common to all high power accelerator initiatives, is the feasibility and availability of materials that can meet the ever-increasing demand of power. Recent irradiation damage studies (BNL experiment E951) showed that special materials exhibiting superb behavior in the non-irradiated state lose their distinct properties very rapidly with radiation. Results of these studies, combined with the requirements of recent accelerator initiatives (i.e. BNL Neutrino Superbeam), prompted the idea of focusing attention on a narrow material matrix and answering questions regarding the serious implications a material choice might have when used as an accelerator target as it experiences irradiation damage and severe shock.

To reach the goal, materials need be selected based on a figure of merit which combines the material Z value with properties like conductivity, coefficient of thermal expansion, fracture toughness, etc. Specimens appropriate for the experiment, the available apparatus and the facility constraints are to be designed and fabricated then irradiated with the 200 MeV protons in order to reach irradiation damage of approximately 0.25 displacements-per-atom (dpa). Specimens are to be allowed to "cool-down" and then transferred to the BNL Hot Cell facility for activation measurements and post-irradiation testing. Through a series of tests, the irradiation effects on (a) mechanical properties such as loss of ductility, failure load and stress-strain relationship, (b) coefficient of thermal expansion and conductivity, and (c) degradation of the special surface treatment of aluminum will be assessed. A material shock experiment using a high power laser is to be performed alongside the irradiation and post-irradiation studies.

Collaborators contributing in this effort are, Dr. Harold Kirk (BNL), Dr. Hans Ludewig (BNL), Dr. Peter Thieberger (BNL), Dr. Leonard Mausner (BNL), Prof. Kirk McDonald (Princeton U.), Dr. John Sheppard (SLAC) and Dr. Kojii Yoshimura (KEK, Japan).

TECHNICAL PROGRESS AND RESULTS:

In FY 2004 the following have been achieved:

- The material test matrix was identified. It includes a 3-D weaved carbon-carbon composite, a new graphite grade (IG-43), the multifunctional alloy "GUM METAL", the composite AlBeMet, Berrylium, Vascomax, Titanium alloy, and nickel-plated aluminum.
- Test specimen design and material specification reports were completed. Vendors were selected and fabrication of the approximately 400 tight-tolerance specimens was completed.
- Irradiation at the BNL BLIP facility has been completed.
- An experiment for establishing irradiation temperatures based on Thermal Sensitive Paint (TSP) techniques, including benchmark simulations, was completed.
- Radiographic analysis of nickel films embedded in the test set-up for beam parameter assessment was performed.
- Activation measurements, with the exception of the 3-D carbon composite and the aluminum, have been completed.
- Mechanical testing of non-irradiated specimens, including some irradiated Vascomax and Titanium alloy specimens, has been performed.
- A Class IV Nd:YAG laser has been interfaced with an ultrasonic system for shock generation and measurements. Preliminary tests were performed.

The following are planned tasks for FY 2005:

- Completion of the mechanical testing for all materials and specimens
- Completion of material physical property changes measurements (thermal expansion coefficient and conductivity).
- Completion of surface bonding degradation assessment for nickel-plated aluminum.
- Completion of the laser-induced shock tests and assessment of its potential use.
- Comprehensive assessment based on the complete results of the experiment.

SPECIFIC ACCOMPLISHMENTS:

Refereed Journals/Refereed Proceedings:

"Material Studies for Pulsed, High Intensity Proton Beam Targets," N. Simos, et al., ASME Proc. Trans., Paper No. ICONE12-49441, 2004.

"Very High Flux Steady State Reactor and Accelerator Based Sources," Ludewig, H., Simos, N., et al., ASME Proc. Trans., Paper No. ICONE12-49442, 2004.

"Target Material Irradiation Studies for High-Intensity Accelerator Beams," N. Simos, et al., Nuclear Physics B (Proc. Suppl.), Elsevier, 2004 (to appear).

This LDRD study contributed to the reports:

"The AGS Based Super Neutrino Beam Facility Conceptual Design Report," BNL 73210-2004-IR, 2004.

"Studies of a Target System for a 4-MW, 24 GeV Proton Beam," CERN-INTC-2004-016, INTC-P-186, April 2004.

Five (5) LDRD-relevant presentations at international meetings have been made.

A funding commitment through the US-Japan Collaboration (Accelerator R&D) of $45K per year has been made (FY04- FY06). Also, proposals to (a) NASA for multi-functional material irradiation at $300K per year for three years, and (b) US LHC Accelerator Program at $100K per year for two years have been submitted.

LDRD FUNDING:

FY 2004	$82,747
FY 2005 (budgeted)	$125,000

Hydrogen Storage Using Complex Metal Hydrides for Fuel Cell Vehicles

James Wegrzyn *04-104*

PURPOSE:

The purpose of this study is to build upon the expertise and unique capabilities at BNL in the development of a practical hydrogen storage system for fuel cell vehicles. The goal is to enhance our fundamental understanding of both the kinetics and thermodynamic properties of complex metal hydrides and their mixtures. This knowledge can then be used as a foundation to respond to both the President's and Brookhaven's Hydrogen Initiatives.

APPROACH:

The renewed interest in the "concept of a hydrogen economy" provides the motivation for this study. The approach is to synthesize and test novel hydrogen storage materials. Materials of interest have been aluminum hydride, alkali hydrides and alanates. The role titanium plays as a catalyst has also been investigated.

TECHNICAL PROGRESS AND RESULTS:

Technical progress was realized for this past year in three areas: 1) the kinetic properties of aluminum hydride, 2) the thermodynamic properties of various complex metal hydrides and 3) the functionality of the titanium catalyst.

The potential of using aluminum hydride as a hydrogen storage medium has been explored, in which accelerated desorption rates have been measured by the addition of small levels of alkali metal hydrides. DOE's 2010 gravimetric and volumetric system targets can be met, but off board regeneration of spent Al back to AlH_3 still needs to be addressed.

The thermodynamic properties of various complex metal hydrides have been investigated. The alanates (Na_2LiAlH_6, $KAlH_4$, K_3AlH_6, K_2NaAlH_6, etc.) were synthesized by mechanical alloying and the enthalpy and entropy of decomposition was determined by measuring pressure-composition isotherms. Preliminary results demonstrate that the equilibrium pressures can be changed substantially by partial substitution of the alkali metal. A better understanding of the thermodynamic effects of alkali-metal substitutions may lead to the development of new classes of high-capacity alanates with thermodynamic properties that are more favorable for polymer electrolyte membrane fuel cell applications.

At the NSLS, Ti *K*-edge x-ray absorption near-edge spectroscopy was used to determine the Ti valence and coordination in Ti-activated sodium alanate. These results demonstrated that the formal titanium valence is zero in doped sodium alanate and nearly invariant during H_2 cycling. A qualitative comparison of the edge fine structure suggests that the Ti is present on the surface in the form of amorphous $TiAl_3$.

SPECIFIC ACCOMPLISHMENTS:

Presentations:

1) Hydrogen storage: Alanates. J. Graetz, J. Reilly, J. Johnson, A. Y. Ignatov, and T. A. Tyson, Battelle Fuel Cell Strategy Meeting, Salt Lake City, UT, 2004.

2) X-ray absorption study of Ti-doped sodium aluminum hydride. J. Graetz, A. Y.

Ignatov, T. A. Tyson, J. Reilly, and J. Johnson, Materials Research Society Fall Meeting, Boston, MA, Nov. 29-Dec. 3, 2004.

3) Hydrogen driven metallurgical reactions (HDMR) to produce reactive, nano-scale and nano-composite materials. J. Reilly, J. Johnson, J. Graetz, R. Klie, G. Sandrock, and J. Wegrzyn, Materials Research Society Fall Meeting, Boston, MA, Nov. 29 - Dec. 3, 2004.

4) New Reversible Complex Hydride Storage Systems. J. Graetz and J. Reilly, Materials Research Society Fall Meeting, San Francisco, CA, Mar. 28 - Apr. 1, 2005.

5) Metal Hydrides, Materials R&D, Heat Transfer & Engineering. J. Reilly (invited panelist) IPHE International Conference on Hydrogen Storage; Lucca, Italy, June 20-22, 2005.

Publications:

1) X-ray Absorption Study of Ti-activated Sodium Aluminum Hydride. J. Graetz, A. Y. Ignatov, T. A. Tyson, J. Reilly, and J. Johnson, Appl. Phys. Lett., 85 500 (2004).

2) Accelerated Thermal Decomposition of AlH_3 for Hydrogen-fueled Vehicles. G. Sandrock, J. Reilly, J. Graetz, W. Zhou, J. Johnson, J. Wegrzyn, Appl. Phys A, accepted Nov. 22, 2004.

Invention Disclosure:

BNL No. 0423 - Metallurgically Stimulated Aluminum Hydride

Responded to the President's Hydrogen Initiative calls which include the DOE-EERE Grand Challenge and the DOE-BES FY 2004 Hydrogen Solicitation.

LDRD FUNDING

FY 2004	$ 70,265
FY 2005 (budgeted)	$110,000

Appendix A

2005 Project Summaries

Appendix A
BNL FY 2005 Projects

(05-003) Full Power Test of the Amplifier for the Optical Stochastic Cooling using JLAB FEL
V. Yakimenko (FY 2005 Funding $120,000)

Test an optical amplifier that would be suitable for optical stochastic cooling (OSC) at the Relativistic Heavy Ion Collider (RHIC).

(05-005) Study of Photon Coupling to an Electromagnetic Field Gradient
C. Scarlett (FY 2005 Funding $132,000)

Develop an understanding of the rotation of a photon's polarization vector which is observed to be approximately two orders of magnitude above the dellipsometer predicted sensitivity.

(05-006) Heavy Ion Physics with the ATLAS Detector
H. Takai (FY 2005 Funding $102,591)

The ATLAS collaboration is exploring its detector potential to carry out a heavy ion physics program. Further simulation studies and heavy ion specific analysis tools need to be developed.

(05-017) Superconducting Lead Photoinjector
J. Smedley (FY 2005 Funding $118,000)

Investigate the photoemission properties of lead with the goal of improving the capabilities of superconducting electron sources.

(05-020) Controlled Formation of Nanostructured RuO2 Catalysts
P. Sutter (FY 2005 Funding $115,000)

Propose experiments using real-time low-energy electron microscopy to establish the oxidation pathway of Ru(0001) and formation of epitaxial RuO_2(110)/Ru(0001), an important model catalyst for CO oxidation reactions.

(05-021) Hydrogen Storage in Complex Metal Hydrides
T. Vogt (FY 2005 Funding $125,000)

Synthesize and characterize single crystals, e.g. of $NaAlH_4$, to provide experimental control of the hydrogen ad- and desorption process and use them as samples for determining basic property data.

(05-028) Behavior of Water on Chemically Modified Semiconductor Surfaces: Toward Photochemical Hydrogen Production
E. Fujita (FY 2005 Funding $120,000)

Study both the absorption of water on well-defined single crystal surfaces of TiO_2 and $SrTiO_3$ and the reaction of the adsorbed water with and without irradiation using photoemission, x-ray

absorption spectroscopy, Scanning Tunneling Microscopy, time-resolved x-ray diffraction, and Density Functional Theory.

(05-030) Assembling of Biological and Hybrid Complexes on Surfaces
O. Gang (FY 2005 Funding $140,000)

Investigate fundamental aspects of self-assembly and to use the resulting knowledge to develop reliable means for assembling biological, inorganic, organic and hybrid complexes into well organized, two-dimensional structures.

(05-033) Ultra High Resolution Photoelectron Spectrometer
P. Johnson (FY 2005 Funding $66,937)

Construct a completely new type of photoelectron spectrometer, which will have unprecedented energy and momentum resolution that will be ideally matched to future light sources such as NSLS II.

(05-038) Metal-Metal Oxide Electrocatalysts for Oxygen Reduction
M. Vukmirovic (FY 2005 Funding $99,000)

Investigate Pt submonolayers on single crystal surfaces of the non-stoichiometric Na_xWO_3 oxide (sodium tungsten bronze), tin oxide, and on $CoWO_4$ and $NiWO_4$ tungstates as a new class of metal/metal oxide electro-catalysts for oxygen reduction reactions.

(05-041) Multifunctional Nanomaterials for Biology
S. Wong (FY 2005 Funding $125,000)

Explore the use of carbon nanotubes as a platform for integrating biological specificity with physical function such as fluorescence or conductivity.

(05-042) Polariton-Enhanced FRET for Device-Integration of Plasma Membranes from Rhodobacter Sphaeroides
P. Abbamonte (FY 2005 Funding $80,000)

Explore methods for nondestructively depositing light harvesting complexes on surfaces, as well as enhancing absorption and long-range donor-acceptor interactions via coupling to surface plasmon polaritons in metal substrates.

(05-044) Intense THz Source & Application to Magnetization Dynamics
G. L. Carr (FY 2005 Funding $100,000)

Use accelerator-based ultrafast Terahertz short magnetic field pulses to examine the magnetization dynamics of a range of hard ferromagnets, starting with Co-Pt alloys and multilayers.

Appendix A
BNL FY 2005 Projects

(05-048) Nano-Imaging of Whole Cells with Hard X-Ray Microscopy
L. Miller (FY 2005 Funding $80,000)

Develop 3-dimensional, high-resolution, hard x-ray imaging techniques for the study of whole living cells and the development of unique nanoscale probes with superior spatial resolution and penetration depth, which will be a strong complement to the existing imaging techniques at the NSLS.

(05-050) Study to Convert NSLS VUV Ring to Coherent IR Source
B. Podobedov (FY 2005 Funding $130,000)

An important aspect of NSLS-II is to address the future needs of IR users via building a separate small ring rather than accommodating them in the new ultra-low emittance 3GeV ring. Will explore this exciting possibility experimentally and by computer simulations.

(05-051) Superconducting Undulator Technology
G. Rakowsky (FY 2005 Funding $190,000)

Attain high peak magnetic fields that cannot be achieved with conventional NbTi superconductors; develop thermal management of the unprecedented high cryogenic heat loads expected in SCU's in future light sources; develop active field error correction means, to minimize electron trajectory and optical phase deviations.

(05-057) Characterization and Imaging of Amyloid Plaques Using Diffraction Enhanced Imaging
Z. Zhong (FY 2005 Funding $100,000

Explore Diffraction Enhanced Imaging (DEI) for early detection of amyloid b peptide deposition, a hallmark feature in Alzheimer's disease and exploit DEI as a novel radiography method that introduces fine selectivity for the angular deviation of x-rays traversing the subject.

(05-058) Development of Methodologies for Analyzing Transcription Factor Binding in Whole Genomes
C. Anderson (FY 2005 Funding $129,300)

Combine Genome Signature Tags (GST) methodology with another technique called chromatin immunoprecipitation (ChIP) to identify the specific loci in human DNA to which the p53 transcription factor binds.

(05-063) Application of Endophytic Bacteria to Improve the Phytoremediation of TCE and BTEX using Hybrid Poplar
D. van der Lelie (FY 2005 Funding $220,000)

Change endophytic bacteria into natural biocatalysts, so that they will improve the degradation of organic pollutants that are taken up by their host plant.

Appendix A
BNL FY 2005 Projects

(05-064) Design and Build Two Dimensional Proten-Lipid Thin Film: A First Step Toward Novel Biochips
Y. Wei (FY 2005 Funding $60,000)

Perform structural and functional studies of metal transporter proteins and develop the technique to "polymerize" these proteins in their fully functional states into a two dimensional matrix in order to form biochips that can be designed to perform reactions or detections with high quality and efficiency.

(05-068) Positron Labeled Stem Cells for Non-Invasive PET Imaging Studies of In-Vivo Trafficking and Biodistribution
S. Srivastava (FY 2005 Funding $135,000)

Develop methods for radiolabeling progenitor stem cells for noninvasively tracking their behavior and fate in vivo through PET imaging, and thus help elucidate their overall role in organ and tissue regeneration in disease states.

(05-069) Breaking the Millimeter Resolution Barrier in fMRI
D. Tomasi (FY 2005 Funding $110,000)

Develop: a) 32-channel radio frequency (FR) phased arrays using high temperature superconductors (HTS), and b) a 32-channel nuclear magnetic resonance (NMR) receiver to massively record parallel datasets at high speed in order to obtain massive partially parallel acquisition techniques to speed up MRI acquisition, making possible functional studies of the human brain at the columnar (submillimiter) scale.

(05-070) Novel Multi-Modality MRI and Transcranial Magnetic Stimulation to Study Brain Connectivity
E. de Castro Caparelli (FY 2005 Funding $112,000)

Develop a revolutionary methodology integrating transcranial magnetic stimulation and simultaneous acquisition of functional MRI, diffusion weighted imaging and diffusion tensor imaging, using BNL's 4T MR scanner, so as to provide unique windows on brain function and connectivity.

(05-071) Ovarian Hormone Modulation of ICP: MRI Studies
A. Biegon (FY 2005 Funding $108,200)

Adapt and validate a non-invasive, MRI based method of measuring intracranial pressure (ICP) recently developed for use with the BNL 4T magnet followed by a study of changes in ICP in women as a function of ovarian hormone status.

Appendix A
BNL FY 2005 Projects

(05-072) Feasibility of CZT for Next-Generation PET Performance
P. Vaska (FY 2005 Funding $110,000)

Evaluate cadmium zinc telluride (CZT) as a detector material for PET applications, as the CZT has the potential to be the driving force for a new generation of high performance PET cameras.

(05-074) Biology on Massively Parallel Computers
J. W. Davenport (FY 2005 Funding $170,000)

Develop new algorithmic approaches for computational biology on massively parallel computers in order to make effective use of machines such as the 10,000 processor Quantum Chromodynamics on Chip and the 131,00 processor BlueGene/L.

(05-078) Ionic Liquids in Biocatalysis and Environmental Persistence
A. J. Francis (FY 2005 Funding $100,000)

Investigate the role of Ionic liquids in enhancing the enzymatic activity with potential applications in industrial, agricultural, environmental and energy generation processes leading to the development of new or improved methodologies.

(05-082) Single Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT-MS) Enhancements: Aerosol Optical Properties and Increased Particle Detectivity
G. Senum (FY 2005 Funding $100,000)

Employ the Single Particle Laser Ablation Time-of-Flight Mass Spectrometer) to measure the index of refraction and absorptivity of aerosol particles.

(05-088) Transition Metals in Oil and Gas Exploration
A. Vairavamurthy (FY 2005 Funding $130,000)

Explore experimentally the potential mechansims for forming zero-valent transition metals under conditions relevant to late diagenetic and catagenetic sediments in order to test the hypothesis that reduced sulfur compounds can react with oxidized transition metal ions, such as Ni(II), to produce the zero-valent state of the corresponding element.

(05-092) An Innovative Infiltrated Kernel Nuclear Fuel (IKNF) for High-Efficiency Hydrogen Production with Nuclear Power Plants
J. Saccheri (FY 2005 Funding $132,000)

Demonstrate the feasibility of an innovative nuclear fuel, the Infiltrated Kernel Nuclear Fuel (IKNF), with has the very high potential of outperforming fuels currently under study for hydrogen production with the Very High Thermal Reactor (VHTR) system.

Appendix A
BNL FY 2005 Projects

(05-094) Development of Green Processes: Catalytic Hydrogenation in Water Utilizing In Situ Biologically-Produced Hydrogen
D. Mahajan (FY 2005 Funding $276,000)

Use Thermotoga neapolitana, a thermophylic bacterium of the order Thermotogales that is able to produce clean (CO-free) hydrogen gas from a variety of carbon sources as a biological hydrogen production strategy using a thermophylic microorganism with a hydrogenation process that uses a homogeneous chemical catalyst that operates in an aqueous solution.

(05-098) Fast Neutron Imaging Detector
J. Lemley (FY 2005 Funding $125,000)

Demonstrate feasibility of a directionally sensitive detector for fast neutrons that has practical detection sensitivity at ranges to 50 meters and greater and could be used to search large areas for improvised nuclear explosive devices (IND), or nuclear materials that could be used to manufacture INDs.

(05-104) Giant Proximity Effect in High-Temperature Superconductors
I. Bozovic (FY 2005 Funding $268,000)

Investigate systematically the Giant Proximity Effect (GPE) in high-temperature superconductors (HTS) by using a state-of-the-art atomic-layer-by-layer molecular beam epitaxy system which allows the synthesis of atomically perfect HTS films and fabrication of precise multilayers and super-lattices with one-unit cell thick HTS or spacer layers.

(05-105) Development of an Observation-based Photochemical-Aerosol Modeling System
D. Wright (FY 2005 Funding $108,000)

Elements of two chemical transport models [EPA's Community Multiscale Air Quality (CMAQ) model and BNL's Global Chemistry Model driven by Observation-derived meterology (GChM-O)] will be combined and augmented to form a highly modular related set of observation-based models to represent chemical and aerosol microphysical processes and test those representations in a highly constrained environment.

(05-106) Exploring Root Physiology in Relation to Uptake of Groundwater Pollutants
R. Ferrieri (FY 2005 Funding $165,000)

Provide a foundation for understanding how root physiology, linking solute exchange between roots and shoots of the whole plant with uptake of organic contaminants, can be manipulated to improve CCl_4 assimilation.

Appendix A
BNL FY 2005 Projects

(05-108) X-ray Absorption Spectroscopic Method for Studying Environmentally-relevant Reaction Kinetics
J. Fitts (FY 2005 Funding $93,000)

Combine synchrotron-based microspectroscopy and Quick-scanning X-ray absorption spectroscopy measurements made in parallel on identical samples in order to follow the time-dependent chemical transformations of a metal ion contaminant in a heterogeneous sediment that will enable detailed chemical kinetics studies of contaminant metals and radionuclides as they react with heterogeneous samples.

(05-109) Global Cloud Analysis Technologies (G-CAT)
A. Vogelmann (FY 2005 Funding $93,000)

Architect a framework that would 1) enable the requisite acquisition of voluminous, global data sets from sophisticated surface-based instrumentation and satellites, and 2) explore novel methods for efficiently integrating the information content of data from these diverse sensors.

(05-110) Computational Science
D. Keyes (FY 2005 Funding $121,000)

Develop a new basic parallel algorithms for the efficient solution of larger linear systems, both sparse and dense and in fast Fourier transforms, important for wide range applications.

(05-111) Structural Study of gamma-Secretase by Cryo-EM
H. Li (FY 2005 Funding $210,000)

Apply high-resolution electron microscopy (EM) technique to elucidate the architecture of the entire gamma-secretase complex, and more specifically how the four components physically associate with each other to form the complex and how the complex interacts with various substrates.

(05-112) Structural Analysis of Bacterial Pilus Biogenesis
H. Li (FY 2005 Funding $210,000)

Apply high-resolution electron microscopy techniques to elucidate the structural basis of secretion in Gram-negative bacteria by focusing on the chaperone/usher pathway that is dedicated to the assembly and secretion of a superfamily of virulence-associated surface structures.

(05-114) Study of High-T_c Nanostructures
I. Bozovic (FY 2005 Funding $268,000)

Investigate systematically the effects of reduced dimensionality and confined geometries on high-temperature superconductors (HTS) that permit an elucidation of the most basic questions in the HTS physics by using a state-of-the-art atomic-layer-by-layer molecular beam epitaxy

system that permits the synthesis of atomically smooth HTS films, multilayers and superlattices that contain one-unit cell thick HTS layers.

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 20, 2004*

to: *Distribution*

from: *L. Newman L.N.*

subject: *Laboratory Directed Research & Development Program (LDRD) Proposals*

We are now soliciting proposals for the annual LDRD competition. Proposals must be submitted by April 5, 2004, through your respective Chairperson and Associate Laboratory Director to the Administrator for LDRD (Kevin Fox in Bldg. 460). The revised version of the Proposal Information Questionnaire (PIQ) submission form must be used, and it can be obtained electronically by going to https://sbms.bnl.gov/standard/3c/3c02e011.htm or from greco@bnl.gov. A copy is attached for your convenience. 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 that is not more than three pages in length. Also, note that LDRD projects are restricted to a maximum of three years. However, projects and their budgets should be tailored to no more than a two-year schedule. Along with your proposal you are requested to include a one-page vita and 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 each year there is a mid- year review of all programs to assess the extent of progress.

Research conducted under the LDRD Program should be highly innovative, and an element of high risk as to success is acceptable. This year we will be especially pleased to receive innovative new projects in the general areas of the Life Sciences, and at the Interface of the Life and Physical Sciences, as we will be allocating up to 50% of the available funds for these areas. *Examples* of the former include brain imaging, plants systems biology, and computational biology. *Examples* of the latter include biosensors, nano/biomaterials synthesis, and computational modeling. The total amount for new starts in FY 2005 has not yet been determined, but we expect it to be in excess of 3.5 million dollars.

The Selection Committee will be chaired by the Scientific Director for LDRD and includes the Deputy Director for Science and Technology along with the Associate Laboratory Directors and

is augmented by selected distinguished scientists. The committee hopes to conclude the selection process by the end of June.

For your convenience and planning purposes, note the following calendar for LDRD activities.

February 20, 2004	Call for FY 2005 Proposals
April 5, 2004	FY 2005 Proposals Due
May 3 – 7, 2004	FY 2004 Mid-Year review
May 25 – June 30, 2004	Selection of FY 2005 Projects
August 15, 2004	FY 2005 Plan Due to DOE
October 1, 2004	Funding of FY 2005 Projects
October 10, 2004	Call for FY 2004 Annual Reports
November 12, 2004	FY 2004 Annual Reports Due

LN:kjf
Attachment

Distribution:
Level I & II Managers

cc: N. Narain

K:\LDRD\FY 2005\call memo Directorate FY2005.doc

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/ldrd/) 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? Y/N _____

If **yes**, has approval from BNL's Animal Care and Use Committee been obtained? 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 Select Basic or 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 (List names, type of staff, and level of effort, and where names are not known indicate TBD) 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			
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.