

**Laboratory Directed
Research & Development
Program Activities
For FY 2008**

Annual Report

**BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
UPTON, NEW YORK 11973-5000
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Introduction projects

Brookhaven National Laboratory (BNL) is a multidisciplinary laboratory that maintains a primary mission focus in the physical sciences, energy sciences, and life sciences, with additional expertise in environmental sciences, energy technologies, and national security. It is managed by Brookhaven Science Associates, LLC, (BSA) under contract with the U. S. Department of Energy (DOE). BNL's Fiscal year 2008 budget was \$531.6 million. There are about 2,800 employees, and another 4,300 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 413.2B, "Laboratory Directed Research and Development," April 19, 2006, and the Roles, Responsibilities, and Guidelines for Laboratory Directed Research and Development at the Department of Energy/National Nuclear Security Administration Laboratories dated June 13, 2006. Accordingly, this is our Annual Report in which we describe the Purpose, Approach, Technical Progress and Results, and Specific Accomplishments of all LDRD projects that received funding during Fiscal Year 2008.

BNL expended \$12 million during Fiscal Year 2008 in support of 69 projects. The program has two categories, the annual Open Call LDRDs and Strategic LDRDs, which combine to meet the overall objectives of the LDRD Program. Proposals are solicited annually for review and approval concurrent with the next fiscal year, October 1.

For the open call for proposals, an LDRD Selection Committee, comprised of the Associate Laboratory Directors (ALDs) for the Scientific Directorates, an equal number of scientists recommended by the Brookhaven Council, plus the Assistant Laboratory Director for Policy and Strategic Planning, review the proposals submitted in response to the solicitation. The Open Call LDRD category emphasizes innovative research concepts with limited management filtering to encourage the creativity of individual researchers. The competition is open to all BNL staff in programmatic, scientific, engineering, and technical support areas. Researchers submit their project proposals to the Assistant Laboratory Director for Policy and Strategic Planning.

A portion of the LDRD budget is held for the Strategic LDRD (S-LDRD) category. Projects in this category focus on innovative R&D activities that support the strategic agenda of the Laboratory. The Laboratory Director entertains requests or articulates the need for S-LDRD funds at any time. Strategic LDRD Proposals also undergo rigorous peer review; the approach to review is tailored to the size and scope of the proposal.

These Projects are driven by special opportunities, including:

- Research project(s) in support of Laboratory strategic initiatives as defined and articulated by the Director,
- Research project(s) in support of a Laboratory strategic hire,

- Evolution of Program Development activities into research and development activities,
- ALD proposal(s) to the Director to support unique research opportunities.

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. We explicitly indicate that research conducted under the LDRD Program should be highly innovative, and an element of high risk as to success is acceptable.

To be one of the premier DOE National Laboratories, 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.

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2008 PROJECT PROGRAM SUMMARIES

Detector Development for Very Long Baseline Neutrino Experiments

LDRD Project 06-004

Milind Diwan and Sebastian White

PURPOSE:

We are developing new concepts, originated by BNL researchers, for the design of a very large (500 kT) multipurpose Water Cherenkov detector with a broad band accelerator neutrino beam. A large mega-ton scale detector with high electron-neutrino detection efficiency, good energy resolution and background rejection is needed to reach the physics sensitivities of the next generation of very long baseline neutrino experiments and proton decay experiments. We envision placing such a detector deep underground in the proposed Deep Underground Science and Engineering Laboratory (DUSEL) facility which will be located in the former Homestake gold mine.

This LDRD is now completed and it has met all its goals: the above project has been recommended by the High Energy Physics Advisory Panel as one of the key projects for the US particle physics program.¹ Considerable progress has been made in building a collaboration that will produce a Conceptual Design Report by the end of calendar 2009. Much of the scientific, and technical information that was given to the Particle Physics Project Priority Panel (P5) that examined the project in detail for the Department of Energy, was produced with the help of this Brookhaven LDRD. As the project moves forward in the near future, it is very likely that BNL will be called upon to lead the project management of the detector at DUSEL.

APPROACH:

The project originated several years ago when BNL scientists were examining the detection of CP violation amongst neutrinos. CP violation results when neutrinos and antineutrinos do not behave in the same way; in particular the recent discovery of neutrino flavor transformation has led to the idea that the rate of flavor transformation could be fundamentally different for neutrinos and antineutrinos and this difference could be responsible for the predominance of matter over anti-matter in our universe.

As a result of our early work we found that the detection of CP violation in neutrinos was possible with conventional technology, but it needed a very intense beam of neutrinos and a very massive detector to obtain sufficient event rate. We also found that placing the detector far away from the source allowed one to measure both the ordering the 3 neutrino masses (which are unknown at present; only the differences are known), and possible CP violation.²

In this proposal, we decided to further examine the design and costing of a large underground 500 kT Water Cherenkov detector. We chose Water Cherenkov as the initial detector technology to consider due to the proven track record of such detectors in neutrino and proton decay physics. Currently, the largest such detector built is the SuperKamiokande detector which is 50 kT.

¹ http://www.er.doe.gov/hep/HEPAP/reports/P5_Report%2006022008.pdf

² M. Diwan et al., Very long baseline neutrino oscillation experiments for precise measurements of mixing parameters and CP violating effects, *Phys. Rev. D* **68**, 012002 (2003). <http://nwg.phy.bnl.gov>. Also see M. Diwan, The Case for a Super Neutrino Beam, Heavy Quarks and Leptons Workshop 2004, San Juan, Puerto Rico, 1-5 Jun 2004. Archive: [hep-ex/0407047](http://arxiv.org/abs/hep-ex/0407047).

Ultimately, we will need a detailed design of a large detector with mass greater than 100 kT. We focused on 3 areas for this detector: 1) detailed simulations and calculations of the event rates and sensitivity, 2) preliminary examination of the design, cost, and schedule of the cavern needed to house such large detectors in the DUSEL, 3) examination of candidate photomultiplier tubes for the project with emphasis on their pressure resistance under water.

TECHNICAL PROGRESS AND RESULTS:

Earlier progress from this work was reported in a complete report to the NuSAG (Neutrino Scientific Advisory Panel) in 2007.³ A large number of presentations to various conferences and committees followed. For this year we have reexamined the physic sensitivities of the experiment (see Fig. 1). A more detailed cavern engineering plan has been created (Fig. 2 and Fig. 3). The schedule for such a plan has been examined by an experienced underground mining consultant. Briefly, the cavern can be excavated in <5 years, but needs an initial 1-2 year geotechnical site investigation (attempts are under way to fund such a site investigation from the NSF; the funds will, however, be supplied to the DUSEL facility team at Berkeley and South Dakota). Lastly, Fig. 4 shows our pressure tests of several Hamamatsu R7081 photomultiplier tubes. The candidate photomultipliers must be able to withstand at least 74 psi(5 atm) of pressure. As a result of this LDRD, the pressure performance has been demonstrated. Feasibility of all important elements of this detector has been now demonstrated. A newly formed collaboration intends to create a Conceptual Design Report in 2009.

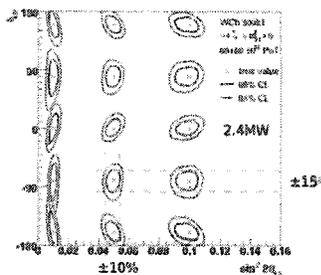


Fig. 1 The expected parameter resolution for a 300kt detector and 2.4 MW beam from FNAL.

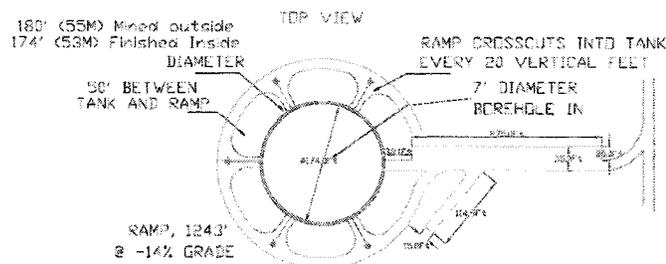


Fig. 2. Detailed top view of the detector chamber excavation plan at the 4850 ft level.

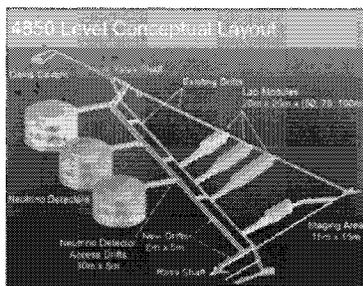


Fig 3. The layout of 3 chambers at the 4850 ft level in Homestake mine.

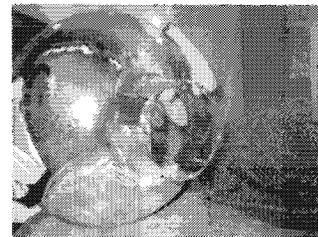
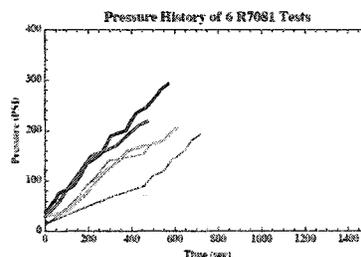


Fig. 4. Pressure performance of 6 R7081 PMTs (left). Pressure was raised until the tube imploded (right).

³ "Report of the US long baseline neutrino experiment study". V Barger et.al., FERMILAB-0801-AD-E, BNL-77973-2007-IR, May 2007. e-Print: arXiv:0705.4396

Detector for High Quality Images of Electron Microscopy

LDRD Project 06-012

P. Rehak, G. Deptuch, J. F. Pratte and J. Fried

PURPOSE:

The technical objective of this LDRD project is to develop an Active Pixel Imager (API) based detector for electron microscopy. The image produced by the sensor under development will be limited only by physics of the electron microscope. The detector will be capable of providing these high quality pictures at frame rates high enough to allow dynamic studies of biological objects and structures in nano-science.

APPROACH:

Detectors are a critical part of any electron microscope, since all the image, diffraction and spectroscopy information must pass through them prior to analysis. A wide range of topics, both in materials science and biology, are currently beyond reach due to limitations in detector technology. Constant progress in semiconductor (silicon) technology is responsible for the recent devices in digital imaging technology called Active Pixel Sensors APSs. These sensors were already designed, produced and tested as detectors of charged particles crossing the plane of sensors. The information being read-out is the total charge released in the active layer of silicon during the whole integration time of the sensor. The number of charged particles crossing the sensor and producing the charge is obtained from the total charge accumulated in individual pixels. These numbers of crossing particles are different from the true numbers due to imperfections of the charge measurement and because of intrinsic fluctuations of the charge produced by the passage of a single particle. Moreover, the dynamic range of the charge measurement limits the dynamic range of the particle count. The proposed detector improves all shortcomings of present APSs.

TECHNICAL PROGRESS AND RESULTS:

Most of the effort during FY 2006 was dedicated to the modeling of the device. The modeling can be divided into two main parts. i) Modeling of the process of the ionization and of the collection of the signal charge within the epitaxial part of the silicon pixel, and ii) amplification of the charge and the signal processing. The process of the ionization produced by the electron beam of the microscope and the collection of the signal charge is not part of any commercially available software. The software to simulate this part of the detection process was developed and used for the optimization of the geometry of the n- and p- wells in the pixels and for the values of voltages to be applied at individual wells. The linear part of the read-out electronics chain was designed with the help of commercial programs for the design of Integrated Circuits (IC).

In FY 2007 the design of a small scale prototype was completed, produced and partially tested. Figure 1 shows the micro - photograph of the produced chip. The large square on the right hand side is a 32 by 32 pixel matrix of independent pixels. Each pixel contains a detection volume followed by the complete chain of read-out electronics. The read-out electronics is formed by a preamplifier followed by a shaper, baseline restorer, comparator and a 15 bit scaler. The pixel architecture of this array is already an exact realization of the architecture to be included in larger arrays intended to be used in electron microscopes.

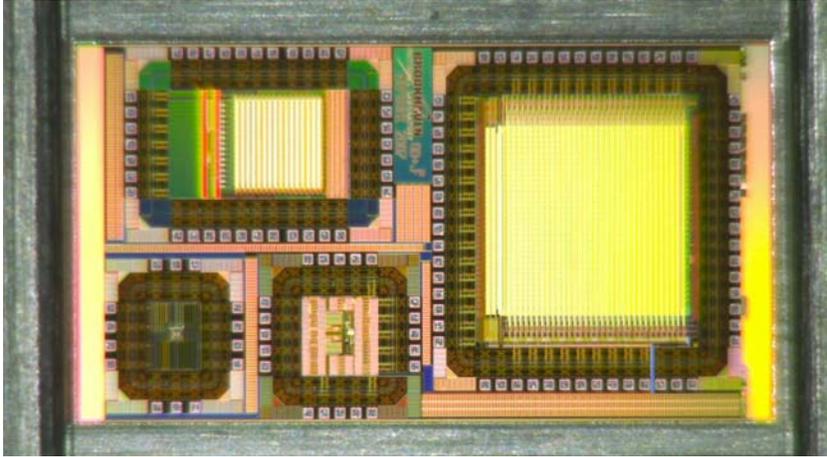


Figure 1. A micro – photograph of the produced chip

In FY 2008 the testing of the chip continued, however, the LDRD effort met with several hurdles; new constraints for bonding of thinned down silicon to a beryllium substrate took effect preventing any preliminary test of silicon – beryllium sandwich. Two of the PIs on this project left BNL. G. Deptuch left BNL in July 2007, and J. F. Pratte left BNL in January, 2009. Therefore, we have proceeded directly to the testing. Therefore we modified the planning of existing arrays within the electron microscopes. We will minimize the risk of missing a design flow by performing more extensive series of tests. We will collaborate closely with physicist at the biology department and at the CFN to carry on these tests.

Transmission Photocathode Development

LDRD Project 06-017

John Smedley

PURPOSE:

The aim of this project is to develop a photocathode which will provide a significant average current while being illuminated in transmission mode. Such a cathode is needed for applications where it is difficult or impossible to illuminate the cathode in reflection mode. One such application of particular importance to BNL is the diamond amplified photocathode project, which would cover the electron-emitting side of the photocathode with a thin diamond layer, forming a capsule (figure 1). This cathode is intended as the electron source for the C-AD Energy Recovery Linac (ERL) project and the e-cooler upgrade that is part of RHIC II. In addition, recent development in the ERL program has created a need for a high quantum efficiency, reflection mode cathode; this goal has been folded into the ongoing research program.

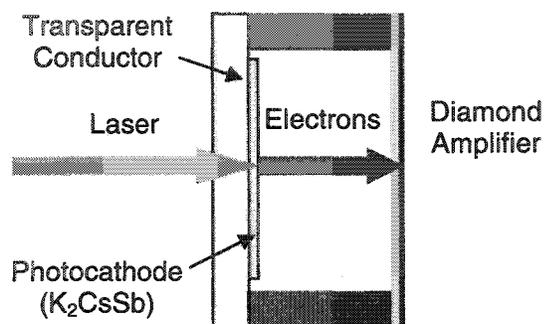


Fig. 1: Capsule with transparent cathode

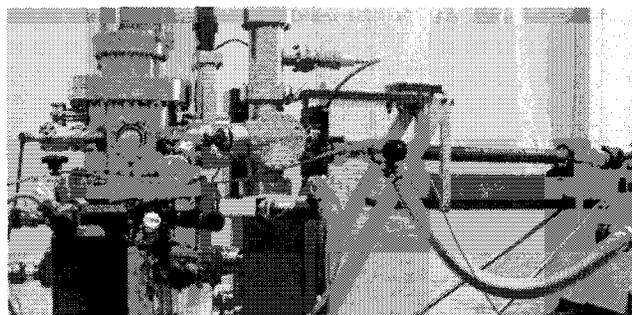


Fig. 2: Deposition system

As shown in the figure, in the transmission mode, the laser light passes through the transparent substrate and a thin conducting layer to irradiate the photocathode at the conductor-cathode interface. The electrons generated by the laser then travel through the cathode material to be emitted from the opposite surface.

Several factors will impact the performance of a transmission photocathode. The substrate must be optically transparent and a good thermal conductor. It must be coated with a layer of sufficient conductivity to provide electron resupply to the photocathode. This layer must also be optically nearly transparent and must be compatible with the photocathode material. The cathode layer should be thick enough to absorb a significant fraction of the laser photons and yet thin enough to transmit a significant fraction of the electrons generated. The resulting photocathode should be able to produce significant average current, and the lifetime at high current will need to be characterized.

APPROACH:

An existing vacuum chamber has been modified to accommodate deposition of antimony, potassium and cesium. A manipulator arm in vacuum allows the cathode substrate to be coated by each source sequentially. The deposition rate of the antimony and potassium sources is measured via a crystal monitor, while the deposition of cesium is controlled by monitoring the photocurrent during deposition. The thickness of the cathode can be monitored after each step via optical transmission. After deposition, the cathode quantum efficiency is monitored by illumination with a laser in either reflection or transmission mode. Emitted current is measured leaving the cathode, and the cathode can be biased to prevent space-charge limiting of the

current. A lamp source with monochromator is also used to illuminate the cathode, allowing the spectral response to be measured. The system can use a wide variety of substrate materials for both reflection and transmission photocathodes.

We are currently studying K_2CsSb . This cathode is used in photomultiplier tubes in transmission mode, and has a high quantum efficiency (QE) for visible light. The deposition recipe will be optimized for high QE in both reflection and transmission modes, by adjusting the thickness of cesium, potassium and antimony used, as well as the substrate temperature during deposition.

TECHNICAL PROGRESS AND RESULTS:

Several reflection mode cathodes have been successfully created during this project, with peak QE well in excess of the ERL machine requirement of 10% at 355nm. Optimization of reflection mode deposition is currently a priority, as changes to the ERL project timeline have led to the determination that the first high-current cathode to be used will be reflection-mode K_2CsSb . Figure 3 shows a collection of the spectral response of the cathodes in reflection mode, along with high-current tests made with a green laser.

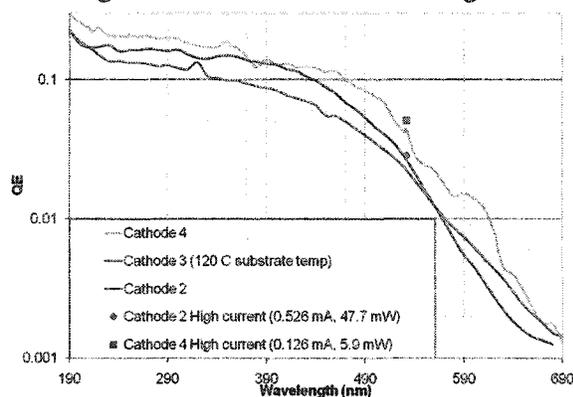


Fig. 3: K_2CsSb Spectral Response

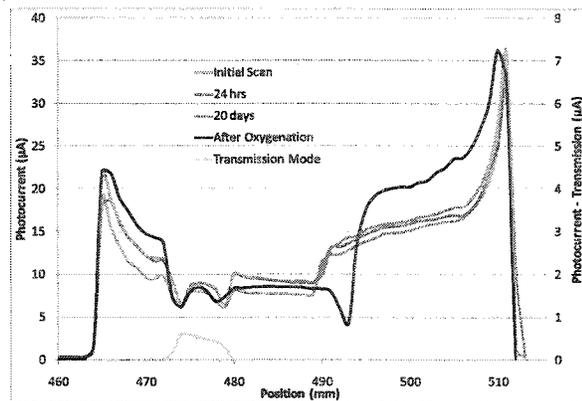


Fig. 4: Spatial uniformity and lifetime

Figure 4 shows spatial scans across cathode 3, in both reflection and transmission mode. The response of the cathode is very uniform on a given substrate – the step difference in the photocurrent at position 493 mm represents a change from a copper substrate to stainless steel (SS), suggesting that SS is a superior substrate material for this cathode. The QE was measured over the course of several weeks of storage, and was unchanged. An attempt was made to further improve the response by superficial oxygenation, with marginal improvement. The transmission mode QE was $\frac{1}{2}$ the reflection mode QE, after accounting for the 80% loss in the copper coating used as a transparent conductor. More recent tests have suggested that Indium-Tin Oxide (ITO) may provide better transmission mode performance; the absorption in ITO is less than 10%, and a cathode deposited on ITO provided nearly the same QE in both reflection and transmission mode.

In summary, this project has succeeded in developing a recipe to create cathodes of sufficient QE to meet the near-term CAD ERL machine requirements for a reflection mode cathode. We have demonstrated current densities in excess of the ERL requirement. Lifetime studies of these cathodes are underway, as well as investigation of methods to further improve the response, such as Cs-O termination and use of other substrates. Work on transparent cathodes is ongoing, with further experiments planned using ITO as a cathode substrate.

Synthesis and Characterization of Band-Gap-Narrowed TiO₂ Thin Films and Nanoparticles for Solar Energy Conversion

LDRD Project 06-021

Eli Sutter, Peter Sutter, Etsuko Fujita and James Muckerman

PURPOSE:

TiO₂ is considered to be the most promising semiconductor material for solar energy conversion into chemical energy (H₂) via photo-decomposition of water because of its high stability, availability, low cost and non-toxicity. Its only disadvantage is being photoactive under ultraviolet (UV) light irradiation [wavelength (λ) < 387 nm] rather than from the main part of the solar spectrum. One promising approach to making TiO₂ highly reactive under visible light is to modify it via substitutional doping with nitrogen, carbon and boron that can lower the energy gap and shift absorption towards longer wavelengths. Under this LDRD project we are developing synthetic routes for the reliable in-situ doping of TiO₂ crystalline thin films and nanoparticles with N, C, and B. We will use the synthesized material for basic research in solar water photoelectrolysis, important aspects of which are understanding of the mechanism of doping and the interaction of H₂O with doped TiO₂.

APPROACH:

We perform epitaxy and doping in our ultrahigh vacuum (UHV) reactive magnetron sputtering deposition system combined with a scanning tunneling microscope (STM) and Auger electron spectrometer (AES). This combination is unique as it allows us to study the synthesized doped material in-situ, without any further surface cleaning or annealing that might introduce changes, using tunneling microscopy and spectroscopy to determine the surface electronic structure and the interaction of H₂O with doped TiO₂. We use state-of-the-art analytical techniques in transmission electron microscopy (TEM) to determine dopant densities and distribution and to evaluate the stability of the doped material.

TECHNICAL PROGRESS AND RESULTS:

In this past year we made major progress in the epitaxial deposition and in-situ doping of rutile TiO₂ thin films using two different gases: nitrogen dioxide (NO₂) and N₂ as source of nitrogen.

(A) *In-situ N-doping of TiO₂ from NO₂*. Following our earlier experiments (first twelve months of this project) on setting-up the epitaxial growth of TiO₂ in our system we made a big step forward by establishing in-situ N-doping. Rutile films were prepared by reactive magnetron sputtering on TiO₂ and Si substrates. Both the undoped and doped rutile TiO₂ films on TiO₂ are high quality single crystalline films. The quality of the surface is excellent with large atomically flat terraces, major prerequisite for understanding the mechanism of N doping. The nitrogen content in the films was measured using electron energy loss spectroscopy (EELS) in the TEM in thick polycrystalline rutile films prepared on Si substrates (Figure 1). TEM images of an undoped and a N-doped TiO₂ films, with thicknesses about 0.2 microns, suitable for electrode material, are shown in Figures 1A and B. The nitrogen content in the N-doped film (Figure 1B) was estimated to be ~ 4 at.%, or TiO_{1.94}N_{0.06}. This level of doping is similar to the levels obtained by doping after the formation of TiO₂. However, in contrast to films doped after formation, in which N-induced structural destabilization occurs, the in-situ prepared material showed excellent stability.

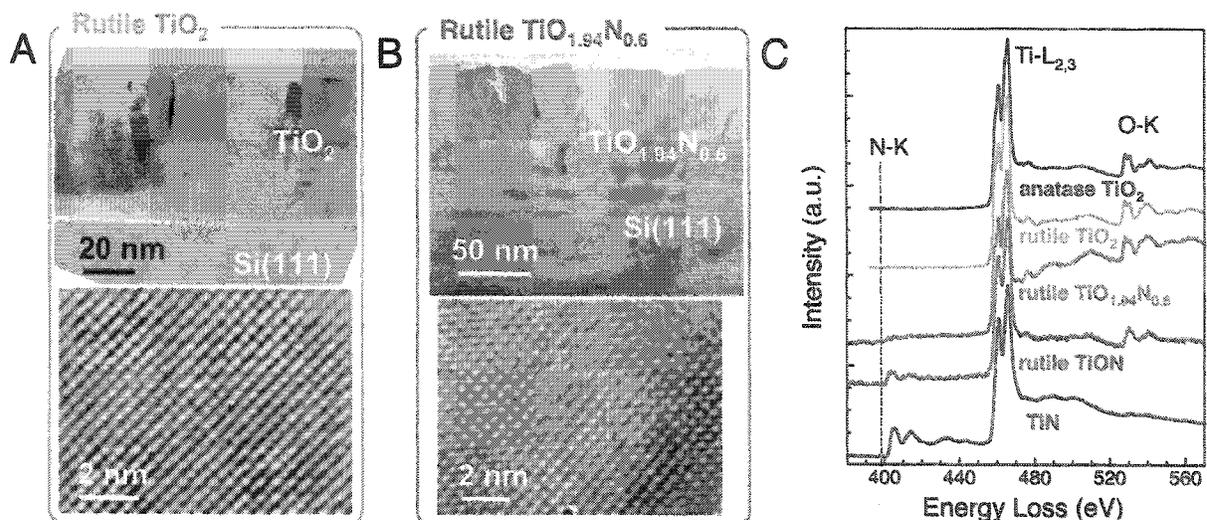


Figure 1: (A) TEM images of an undoped TiO₂ film and (B) TiO_{2-x}N_x film doped from NO₂. (C) EELS spectra of the film in (B) and a TiON film doped from N₂ from which the N content was determined. EELS spectra from TiO₂ and TiN were measured for comparison.

(B) *In-situ N-doping of TiO₂ from N₂*. Series of films were deposited to establish the optimum conditions for incorporation of nitrogen. These efforts led to a major breakthrough, namely formation of stable TiO₂ material doped with large amounts of nitrogen. The films were deposited on rutile TiO₂ (for STM doping mechanism studies) and on Si. It was established that the nitrogen content of the films could be controlled in a very wide range, from light N-doping to formation of stable Ti oxynitride, via the N₂ pressure. The EELS spectrum shown in figure 1C (rutile TiON) is for a TiON film. More importantly the nitrogen content was shown to be uniform over the thickness of the films. The level of doping achieved from N₂ is much higher than doping from NO₂. This is probably due to the preferential oxidation of Ti in the presence of atomic oxygen resulting from the dissociation of NO₂ that competes with the formation of Ti-N bonds. From valence EELS measurements the reduction of the band gap at high level of doping was determined to be ~ 0.2 – 0.3 eV, which would extend the absorption from the UV to the blue part of the solar spectrum, roughly doubling the absorbed photon flux at air mass 1.5 irradiation.

The achievement of substitutional doping of TiO₂ with nitrogen at levels previously thought impossible provides us with unique material. We plan experiments on formation of the doped material and investigation of its properties in our exceptional deposition system with in-situ STM to determine the near surface electronic structure of the doped films and elucidate the atomistic doping mechanism as well as the interaction of the doped TiO₂ with water under controlled UHV conditions.

Development of Gadolinium-Loaded Liquid-Scintillators (Gd-LS) with Long-Term Chemical Stability for a New High-Precision Measurement of the Neutrino Mixing Angle, Theta-13

LDRD Project 06-030

Richard L. Hahn and Minfang Yeh

PURPOSE:

The main purpose of this LDRD to develop gadolinium-loaded liquid-scintillators (Gd-LS) with long-term chemical stability in support of neutrino mixing-angle measurements.

Proposed Main R&D Tasks:

1. To continue evaluation of alternatives to the LS, pseudocumene (PC).
2. To evaluate chemical compatibility of Gd-LS with acrylic (detector vessel).
3. Current R&D is with the new LS, Linear Alkyl Benzene, LAB, an attractive alternative to PC:
 - High flashpoint, 130° C; Biodegradable, environmentally friendly; Readily available from industry, tons produced for detergents; must show is compatible with acrylic
 - We have successfully prepared Gd-LS in LAB. It compares favorably to Gd in PC. Studies needed to determine long-term stability.

APPROACH:

This is an ongoing program to develop metal-loaded LS for a variety of neutrino experiments. The LDRD funding was used primarily to support a postdoc research associate in the group, Dr. Yuping Williamson.

TECHNICAL PROGRESS AND RESULTS:

The goals of our LDRD program were general and research oriented.

1. We applied our expertise in nuclear chemistry to develop methods to assay, reduce, and/or eliminate radioactive contaminants in the materials that we work with.
2. We succeeded in developing an alternative to pseudocumene, PC, namely LAB.
3. We began to study chemical speciation of (trivalent) Ln-MVA complexes to gain understanding of their chemical composition and structure, and the factors that determine their stability; e.g., $\text{Ln}^{(3+)}(\text{RCOO})^{[-(3-x)]}(\text{OH})^{[-x]}$.

MILESTONE

The Daya Bay Project in China passed the DOE CD-2 Level in 2008. Project funding was received from OHEP during the summer of 2008 and support for our postdoc was transferred to the project. At that time, this LDRD ended.

Electronic Properties of Carbon Nanotubes and Novel Multicomponent Nanomaterials

LDRD Project 06-037

John Hill

PURPOSE:

The purpose of this LDRD is to develop an interdisciplinary tool set to understand the electronic properties of organic nanomaterials. These materials are important from both a fundamental and applied perspective, with promising applications in fields such as optoelectronics and photovoltaics. Central to their application in these fields, however, will be a complete understanding of their electronic behavior – the subject of this program.

APPROACH:

The approach taken is a multidisciplinary one, bringing to bear a range of experimental and theoretical tools with a goal of understanding, and ultimately manipulating, the electronic properties of organic nanomaterials. Initial work centered on carbon nanotubes, which are the prototypical example of organic nanomaterials, and which have a wide range of potential applications, particularly photovoltaic uses. More recent work has explored CaC₆, a superconducting graphite intercalation compound.

Experimentally, inelastic x-ray scattering has been used to probe the electronic response of these systems over a range of momentum and energy transfers. These data are combined with electron energy loss, optical conductivity, Raman scattering and ARPES measurements of the same system to provide a complete picture of the electronic excitation spectrum.

Theoretically, first-principles based calculations were performed to evaluate response functions to compare with the experimentally observed spectrum. Furthermore, a serious effort of this project was devoted to the development of novel real-space methods to tackle the electronic excitations. Such real-space approaches provide more natural descriptions and better understandings of organic nanomaterials, which are strongly influenced by the real-space boundaries, and typically do not have periodicity at short length scale.

Collaborators in the nanotube project include D. Casa and T. Gog (ANL), G. Eres and D. Lowndes (ORNL) and R. F. Klie (UIC), Y. Zhu and A. Stein (BNL). Collaborators in the CaC₆ project include A. C. Walters, C. A. Howard, K.C. Ranejat, M. Ellerby and D. McMorrow (UCL), A. Alatas and Bogdan Leu (ANL) and T. Valla. New theoretical developments are also tested with experimental observations performed by B. C. Larson (ORNL), P. Abbamonte (UIUC), and I. Zaliznyak.

TECHNICAL PROGRESS AND RESULTS:

We first investigated the physical parameters controlling the low-energy screening in carbon nanotubes via electron energy loss spectroscopy and inelastic X-ray scattering. Two plasmon-like features are observed, one near 9 eV (the so-called π plasmon) and one near 20 eV (the so-called $\pi+\sigma$ plasmon). At large nanotube diameters, the $\pi+\sigma$ plasmon energies are found to depend on the number of walls and not on the radius or chiral vector. The observed shift with number of walls indicates a change in the strength of the screening and in the effective

interaction at inter-atomic distances; thus this result suggests a mechanism for tuning the properties of nanotubes.

Related to the experimental observations, we have developed a set of real-space theoretical approaches to describe strongly bound excitons commonly found in nano-materials and strongly correlated systems. These include 1) applying first-principles Wannier functions for evaluation/interpretation of the anisotropic momentum-dependence of the spectral weight, 2) formal development of time-dependent density functional theory within LDA+U approximation and its applications to calculation of binding energy and energy spectra of the local Frenkel excitons, 3) a many-body “super-atom” method to incorporate many-body multiplets in strongly correlated charge-transfer insulators, and 4) formal development of kinetic hopping kernel of the excitons to describe the propagation in real space and time.

These new theoretical developments have been applied to real materials in direct comparison with experiments. As an example, our new theory provides a simplest explanation of strongly anisotropic Frenkel excitons found in NiO and demonstrated the feasibility of probing sub-nano-scale excitations using the short wavelength of the X-ray. Similarly, working with BNL neutron group, our new results resolve the long-standing question of the 70% missing spectral weight in magnetic scattering in high-Tc cuprates. It is shown that the weight only appears to be missing due to the use of atomic form factors of Cu that entirely ignores the covalency with O atoms. Analyzed with the form factor from our theory, almost the entire weight were recovered.

As another example, we have demonstrated that within our new framework, the long standing debate of charge-transfer excitons in LiF can be finally resolved, and the exciton can be viewed as an effective Frenkel exciton dominated by a single paricle-hole pair, with its dispersion following a simple cosine function (instead of free particle like q^2 function), due to its strong binding that suppresses beyond-nearest-neighbor hopping. Our new methods also reveal and solve serious deficiencies of the common theoretical treatment of exciton via perturbation theory (so-called Bethe Salpeter equation), which is expected to have a large impact on the community led by the Berkeley group.

In addition, we have continued our work on CaC6, a graphite intercalation compound which was discovered to superconduct below 11.4 K in 2005. We have measured the phonon dispersions in CaC6, and found good agreement with theoretical predictions made by Calandra and Mauri and by Kim et al. These same theoretical calculations fail to predict other experimental (phonon-derived) properties of CaC6 correctly. Thus our experimental verification of the phonon dispersion strongly suggests that it is the electron-phonon coupling that is not well understood in these systems. In order to shed direct light on the electron-phonon coupling, we have begun to look at these samples with angle resolved photoemission. Such measurements should probe the electronic structure and provide a quantitative measure of the electron phonon coupling.

To address the realistic physical effects of the random distribution of Ca intercalants, we have developed an accurate and affordable first-principles Wannier function based method to incorporate scattering and decoherence due to the disorder, beyond mean-field theories currently employed by the community. As a test case, application to Na intercalated cobaltates disputes the current belief that disorder is responsible for the lack of experimental observation of the Fermi surface pockets. We plan to extend this new method to include local electron-phonon

coupling, and apply it to CaB6. We believe that the inhomogeneous nature of the electronic structure and the effectiveness of the electron-phonon coupling might hold the key to answer the current puzzle of unexpected higher T_c of this organic material.

Growth and Characterization of CdZnTe Crystals for Improved Nuclear Radiation Detectors

LDRD Project 06-038

Genda Gu and Aleksey Bolotnikov

PURPOSE:

For the detection of gamma rays, CdZnTe (CZT) is recognized as the best choice of material for room-temperature detector operation. It is quite challenging to grow crystals of CZT because of the high vapor pressures of the constituent elements. So far, no one has managed to grow adequate large and high quality single crystals for a commercial detector application. This project is to develop and demonstrate the ability to fabricate a detector with sufficient energy resolution and efficiency to satisfy the requirements of the best Nuclear Radiation Detectors in the world.

APPROACH:

Because the old single crystal growth method is not able to produce the large and high quality single crystal, we try the new crystal growth methods. The structural defects presented in new crystals have to be studied to further improve their quality.

CMP&MS team develops a new plan to grow single crystals by using the furnaces equipped with the infrared microscopy system. The new infrastructure and a number of optimized processes for crystal growth have been established in CMPMS crystal growth laboratory. Safety requirements will be identified and implemented for this project.

NNSD team will carry the material cauterization experiments, including the measurements of the electrical resistivity, carrier lifetimes, structural quality, and sizes and concentrations of tellurium inclusion in as-grown crystals. In addition, EENS team will fabricate and test the crystals as planar detectors.

TECHNICAL PROGRESS AND RESULTS:

For FY 2007, CPM&MS team has studied the crystal growth mechanisms, such as the effect of growth conditions on solid-liquid interface, crystal micro-structure, formation of Te inclusions, and *etc.* We have grown ten of diameter 1.4 cm ingots and ten of diameter 2cm ingots of Cd_{0.9}Zn_{0.1}Te. NNSD team have done a number of properties measurement on the grown crystals. However, the as-grown single crystals have a low resistivity and low electron mobility and short life time. For FY 2008, our goal is to grow the high resistivity ($\sim 10^{10}$ ohm-cm) and high electron mobility-lifetime products ($\sim 10^{-3}$ cm²/V) of large single crystals of CZT materials.

We have study the crystal growth mechanism of Cd_{1-x}Zn_xTe alloy. We study the effect of In-doping level on the resistivity and electron mobility-lifetime products. We have been successful to grow a number of single crystal ingots with a size of 20 mm diameter and 300 mm (see Fig. 1).

We have grown the high quality single crystals of Cd_{0.9}Zn_{0.1}Te with high resistivity and high electron mobility-lifetime products. The resistivity of the single crystals is 10^{11} ohm-cm which is high enough for all nuclear detector. The electron mobility-lifetime products ($\mu\tau$) of the as-grown single crystals of Cd_{0.9}Zn_{0.1}Te with In-doping is as high as 1.2×10^{-3} cm²/V (see Fig. 2 and Fig. 3).

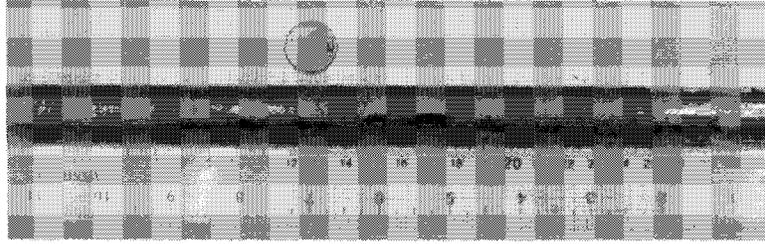


Fig. 1. As-grown indium doped $Cd_{0.9}Zn_{0.1}Te$ single crystal ingot with 20 mm diameter and 30 cm length.

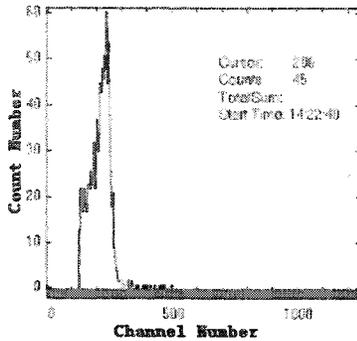


Fig. 2, The spectrum response of an CZT crystal planar detector of $10 \times 10 \times 3.7 \text{ mm}^3$ under 150V from a Am 241 radiation source at 300K.

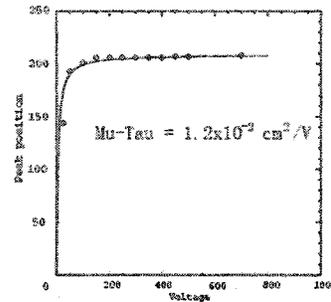


Fig. 3, The electron *Mu-Tau* of an CZT crystal with 6 μs shaping time in the measurement system at 300K. Detector size of $10 \times 10 \times 3.7 \text{ mm}^3$.

The high resistivity of 10^{11} ohm-cm and high *mu-tau* $1.2 \times 10^{-3} \text{ cm}^2/\text{V}$ of the single crystals is one of the best single crystals in the world. We cut these single crystals to make the detectors from the as-grown single crystal ingot rod. A number detectors with various size and shape were made. These include planar detectors and longer cylindrical detectors. These detectors are shown in Fig 4.

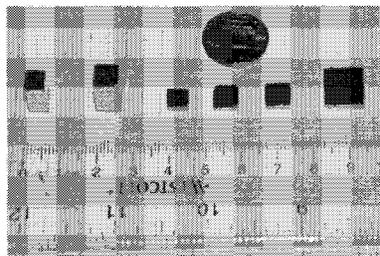


Fig. 4 The various testing detectors made from the one as-grown single crystal ingot.

We have achieved all goals in our LDRD proposal now. The project is successful.

Novel Materials for Hard X-Ray Optics

LDRD Project 06-046

K. Evans-Lutterodt

PURPOSE:

In order to take full advantage of existing and future medium energy synchrotron high brightness x-ray sources, we will need high quality hard x-ray optics with sub-10nm resolution and with high efficiency, to enable the full range of hard x-ray microscopy and spectroscopy techniques that will benefit nano-science. In this project we plan to fabricate high quality kinoform lenses out of silicon and diamond, with an expected impact on the NSLS2 and nano-science at BNL.

APPROACH:

The limiting resolution for an optic is proportional to the $\lambda/(N.A.)$, where N.A. is the numerical aperture of the optic, which is the angular range subtended by the optic as viewed from the focal point. For refractive optics, the numerical aperture of a single lens is limited by the small value of the real part of the refractive index δ , leading to resolutions of order $\lambda/\sqrt{2\delta}$.

In this project we plan to get around this limit by fabricating compound lenses, i.e. an array of single lenses. However, each added lens reduces the overall compound lens transmission. In order not to lose too much intensity as we add lenses to the compound lens, we need to investigate suitable choices of lens materials. One excellent choice might be diamond, in addition to the material currently used which is silicon.

A further obstacle for high resolution hard x-ray optics, is that conventional diffractive optics need to be fabricated with feature sizes that are of the order of the desired optic resolution. In this project we plan to take advantage of one of the features of the kinoform type of optic, which allows one to fabricate optics with feature sizes that can be many multiples of the desired optic resolution, i.e. using a kinoform in higher order. For all choices of materials the major obstacle is the quality of the reactive ion etching, because any deviations from vertical sidewall position result in phase errors in the optics and imperfect lens behavior. So in this LDRD we plan to try to obtain deep reactive ion etching of silicon and diamond wafers, with sidewalls as smooth and as vertical as possible.

TECHNICAL PROGRESS AND RESULTS:

1. Improved Silicon Etching

A new reactive ion etcher was delivered to BNL CFN in October 2006. Abdel Isakovic commissioned the etcher, and then he developed a silicon cryo-etch. On the left is the best etch for silicon that the manufacturer provided for their machine. On the right is an etch developed by Abdel that is substantially better. The sidewalls are vertical, and they are clearly smoother. The publication for this work was *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, Vol. 26, No. 5, pp. 1182–1187, September 2008.

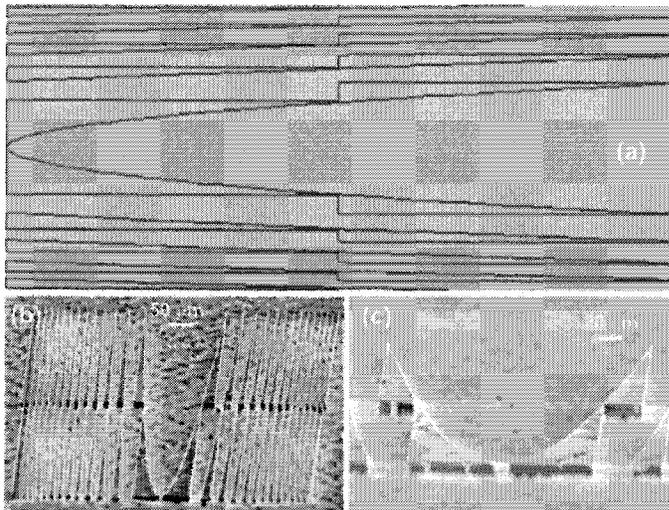
2. Diamond Etching

An etch for diamond has also been developed. Using the cryo-etcher mentioned above, a recipe was developed which was a cyclical oxygen, argon gas process. This has an added benefit of being environmentally friendly. This etch impacted not only our work but also

assisted a different group that is developing high brightness diamond based electron beam sources. This work was included in a conference proceedings publication.

3. Diamond Lens Fabrication

Using the newly developed diamond etch, a diamond lens has been fabricated, as is shown in the Figure below. Here we take advantage of the reduced absorption of the diamond material by fabricating in higher order. This means that the segments are larger than we would usually use for a silicon lens, motivated by the difficulty of diamond fabrication. This lens was tested at the Advanced Photon Source at Beamline 8-ID, and it demonstrated focusing behavior. The results were reported and summarized in Isakovic, A. F., Stein, A., Warren, J. B., Narayanan, S., Sprung, M., Sandy, A. R. & Evans-Lutterodt, K. (2009). *J. Synchrotron Rad.* 16.



Summary

While there were other accomplishments during this LDRD, the main goal was to fabricate and test diamond kinoform lenses. This has been accomplished, and the paper describing this work has been published. Much remains to be done in this primary direction of the LDRD, in particular using single crystal diamond as the lens material.

Nano-Crystallography of Individual Nanotubes and Nanoparticles

LDRD Project 06-047

Christie Nelson

PURPOSE:

The goal of this project is to develop techniques for carrying out x-ray nano-crystallography of individual nanotubes and nanoparticles. X-ray nano-crystallography promises to provide extremely high resolution— on the sub-Angstrom level— for the precise structural characterization of nanomaterials. Since the functional properties of many nanomaterials are determined by their structural properties, this characterization is extremely important. The work on this project is also motivated by the new capabilities that the proposed National Synchrotron Light Source II (NSLS-II) will provide, with focusing down to the nanometer scale. In order to fully take advantage of some of the anticipated NSLS-II capabilities, exploratory work on the feasibility and potential of x-ray nano-crystallography is required.

APPROACH:

In the absence of an existing synchrotron radiation source with the anticipated NSLS-II brightness, the focus of the project to date has been on studies of the radiation damage to nanotubes and nanoparticles. Specifically, the goal is to answer the question of whether or not individual nanotubes and nanoparticles will be able to survive the radiation dose required to result in useful images. To pursue this, the team that includes co-investigators Chi-chang Kao (NSLS), Natasha Bozovic (SJSU), Ivan Bozovic (CMPMS), and James Misewich (CMPMS), and collaborators Haiding Mo (NSLS), Matt Sfeir (CMPMS), Tony Bollinger (CMPMS), Aaron Stein (CFN), Song Jin (UW Madison), Wenjun Liu (APS), Paul Zschack (APS), Zhonghou Cai (APS), and Ken Evans-Lutterodt (NSLS), have studied the radiation damage of carbon nanotubes and metallic nanowires at both the Advanced Photon Source (APS) and the NSLS. Beam time for these studies has been provided through the General User Programs at each facility on microdiffraction beamlines 34-ID and 2-ID at the APS, and on beamline X13B at the NSLS.

TECHNICAL PROGRESS AND RESULTS:

During FY06, radiation damage studies of carbon nanotubes were carried out at the APS. Scanning electron microscope (SEM) images taken before and after the x-ray exposure indicated that these nanomaterials were unable to withstand even a short exposure. These studies also suggested the need for a real-time monitor of sample integrity during future radiation damage studies. Therefore in FY07, real-time studies of nanowire transport during x-ray exposure were conducted. Copper and single-crystal Ni₂Si nanowires were investigated on APS beamline 34-ID and NSLS beamline X13B, respectively. A gradual decrease in the resistance of the copper nanowire was observed over a total exposure of about two days, after which the resistance continued to decrease and then stabilized. No sign of damage was observed through a comparison of SEM images taken before and after the beam time. In Ni₂Si, which is of interest for potential use in microelectronics applications because it can carry a large current density ($\sim 10^8$ A/cm²), the current flowing through the Ni₂Si nanowire was monitored for nearly seven days during x-ray exposure. As with the copper nanowire the resistance was observed to decrease during the x-ray exposure; however in contrast, the resistance recovered its initial value approximately two days after the end of the beam time.

Taken together, the real-time studies of copper and Ni₂Si nanowires indicate that metallic nanomaterials can withstand significant x-ray exposure, and therefore may be suitable for x-ray nano-crystallography experiments. Following up on this, during FY08 we studied a Ni₂Si nanowire using APS beamline 2-ID in an attempt to measure diffraction. This beamline has a Newport kappa diffractometer that enables single-crystal diffraction with monochromatic beam, which is not possible on microdiffraction beamline 34-ID. In addition, the x-ray beam on beamline 2-ID is focused using a zone plate to a $\sim 0.2 \times 0.2 \mu\text{m}^2$ spot, which provides a factor of ~ 6 increase in flux density compared to that delivered at beamline 34-ID. Calculations suggested that this flux would be adequate to observe diffraction from the nanowire.

During the measurements, a fluorescence detector was used to find the Ni₂Si nanowire as it was rastered through the incident beam. A Ni fluorescence map obtained in this manner is shown in the left figure below. Due to the mechanical limitations of the diffractometer, the required scattering geometry resulted in aligning the growth axis of the nanowire orthogonal to the scattering plane. From high-resolution transmission electron microscopy it is known that the growth axis is the [001] crystallographic direction in $\sim 50\%$ of Ni₂Si nanowires, but we had no information about the radial orientation of the nanowire. CCD images were therefore collected over a wide range of sample rotation angles, but there was considerable background scattering and no clear evidence of diffraction from the nanowire was observed. We did, however, observe a decrease in fluorescence from the Ni₂Si nanowire as a function of x-ray beam exposure, as is shown in the middle figure below. We hypothesized that this decrease was due to radiation damage, but post-exposure SEM images, such as the one shown in the right figure below, do not indicate any obvious changes in the appearance of the nanowires.

In conclusion, the development of x-ray nano-crystallography as a probe of individual nanomaterials faces considerable challenges. Radiation damage may not be one of them for metallic nanomaterials, although the resistance changes observed in both copper and Ni₂Si nanowires suggest some x-ray-induced effects that are worthy of further study. X-ray nano-crystallography would clearly benefit from progress on a variety of fronts, including the design of sample substrates or supports that minimize background scattering; improvements in precision sample translation and rotation; increases in beam/thermal stability; optics development for the production of focused white/pink beam; and software development that fully integrates instrument control and data acquisition, and enables real-time analysis of CCD images.

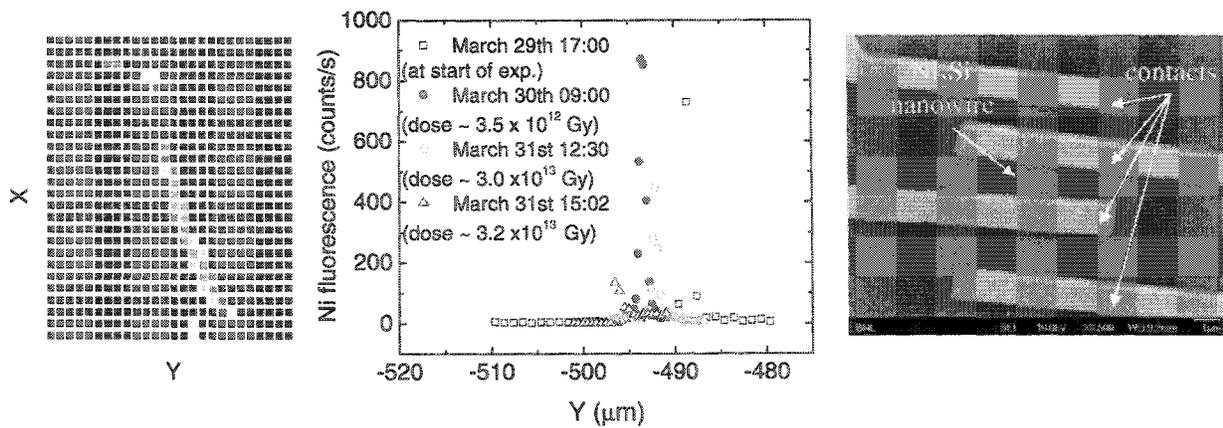


Figure: On the left, a Ni fluorescence map showing the location of the Ni₂Si nanowire. In the middle, Ni fluorescence scans measured over the location of the Ni₂Si nanowire, as a function of x-ray beam exposure. On the right, a post-exposure SEM image of the Ni₂Si nanowire with titanium/gold contacts.

Epigenetics: Methamphetamine (MAP)-Induced Brain Dysfunction and Methylation of DNA

LDRD Project 06-056

John J. Dunn and Panayotis K. Thanos

PURPOSE:

Vertebrate DNA contains about 3.3 billion bases and is heavily methylated at cytosine residues in CpG dinucleotide sequences to form mCpG except for short stretches of CpG-rich DNA, CpG islands or CGIs, about 0.5 to 2 kb long which are normally free of cytosine methylation. Methylation within CpG islands is a common way to regulate nearby gene activity without altering the DNA code. Recent studies have suggested that aberrant methylation within CpG islands which is referred to as an epigenetic modification may play an important role in mediating stable changes in nervous system function including the behavioral changes seen in psychiatric disorders such as schizophrenia. Our hypothesis is that similar changes are probably associated with methamphetamine (MA) associated drug-induced dependence and psychosis. Our goal is to develop methods to detect methylated CpG dinucleotides near genes with clinical relevance following MA treatment of rodents using DNA samples isolated from the nucleus accumbens and other brain tissues. The technology is relevant to developing systems to understand drug addiction, cancer and aging as well as the cellular responses of human cells to low doses of ionizing radiation for DOE's Low Dose Radiation Program. The methodology also is applicable to understanding how cytosine methylation regulates gene expression in plants and is therefore potentially important for future research as part of BNL's initiative to develop sustainable biofuels.

APPROACH:

The major principle behind our work is that largely intact CpG islands with methylated residues can be isolated by exploiting the differential affinity of these DNA fragments for recombinant proteins containing methyl-CpG binding domains. The fragments can then be identified by hybridization to high-density microarrays more recently by high-throughput next generation DNA sequencing methods. Both approaches are being used in our present studies. One disadvantage of current methods is the large (microgram) amounts of template which are required and the need for samples from control tissue. Both would be severe obstacles for follow up studies with precious human samples or with the much smaller brains from genetically engineered mice. To overcome some of these limitations we are developing new improved methods for recovery of methylated-CpG islands followed by analysis on commercially available Nimblegen or Agilent microarrays. As part of this project, we cloned, expressed and purified the *Escherichia coli* McrA protein, a product known to restrict DNA containing mCpG dinucleotides when they occur at Cm5CGG sequences (HpaII sites). This work was published this year in *Protein Expression and Purification*. Under all conditions tested purified McrA does not have measurable nuclease activity on methylated Cm5CGG DNA, although the purified protein does specifically bind HpaII methylated DNA; a result suggesting that McrA may have utility as a reagent for affinity purification of DNA fragments containing mC residues. With this in mind we fused the McrA coding sequence at either the N- or C-termini to an 8 amino acid sequence that enables the fusion protein to bind specifically to a streptavidin matrix. Further experiments showed that the C-terminal fusion could efficiently bind mC containing DNA fragments. N-terminal fusions were not effective in affinity capture presumably due to steric interference between the bound DNA fragments and the matrix. We are currently testing the C-terminal

fusion protein for its utility in detecting aberrantly methylated DNA regions of brain DNA following MA treatment.

TECHNICAL PROGRESS AND RESULTS:

One of the initial aims of this project was to develop an innovative and powerful recombinant protein platform for facile production of high-quality affinity reagents for purification of methylated and non-methylated CGIs. In addition to the McrA protein, we have developed several novel reagents based on Outer Surface protein C from *Borrelia burgdorferi* whose structure was determined here at BNL. OspC has several advantages for these studies including high-expression and solubility in *E. coli* T7-based systems and a coiled-coiled interaction that causes the protein to dimerize without the need for disulfide bonds which imparts a bivalent, antibody-like structure to the OspC recombinant constructions; thereby increasing their binding affinity to CGIs. One of these reagents with an internal run of Histidine residues has been expressed and purified and is now being tested in parallel with our McrA fusion for its ability to detect mCGIs in MA and control animal brain DNA samples. Data analysis is currently in progress. Another important aspect of this project is to develop a new COBRA (Combined Bisulfite Restriction Analysis) method to determine the methylation status of CCGG sequences (i.e., CmCGG vs. CCGG) and to use sensitivity to digestion with HpaII as a simple test of the recognition sequence's internal CpG dinucleotide methylation status in our rodent brain DNA samples. Our plan is to couple both these methods (mC affinity capture and COBRA) to a whole-genome bisulfite sequencing approach to determine the methylation status of cytosines at the single nucleotide level. Briefly, single-stranded DNA is treated with bisulfite which sulfonates cytosine but leaves mC unaffected. The cytosine is then deaminated and desulfonated to uracil. Converted DNA is amplified by PCR with primers designed to amplify only completely bisulfite-modified DNAs and they are directly sequenced and aligned using sophisticated computer algorithms to the unconverted DNA, thus revealing exactly which HpaII sites and nearby cytosines were methylated.

These results will be extended and included, as preliminary data in a grant proposal to NIH/NIDA or DOE.

Molecular Mechanism of Chromosomal Replication Initiation in Eukaryotic System

LDRD Project 06-060

Huilin Li

PURPOSE:

The discovery of the yeast Original Recognition Complex (ORC) was hailed as one of the most important events in cellular chromosomal replication research. However, the operational mechanism of ORC has not been well understood over the past decade due to the lack of structural information. ORC proves to be a difficult target for traditional structure biology method such as x-ray crystallography, because of its multi-component nature and its property of binding to a long stretch of DNA (~ 50 base pairs). Our goal has been to understand how ORC recognizes and marks the cellular chromosomal replication origins, and how ORC helps to initiate replication events by loading the double-strand DNA splitting machinery MCM2-7 helicases through the determination of the molecular architecture of ORC by cryo-electron microscopy (cryo-EM). The BNL LDRD support to this project helps to establish the cryo-EM program in the Biology Department as an important complement to the core strength of NSLS and NSLS-II in biological macromolecular structural biology. This LDRD grant has also helped to successfully attract a 5-year R01 grant from the National Institutes of Health (NIH). This collaborative project with the Stillman group also promotes the scientific exchange and strengthens the tie between BNL and Cold Spring Harbor Laboratory.

APPROACH:

Eukaryotic chromosomal replication is an intricate process that requires the coordinated and tightly regulated action of numerous molecular machines. Failure to ensure once only replication initiation per cell cycle can result in uncontrolled proliferation and genomic instability, two hallmarks of tumorigenesis. The yeast ORC constitutively binds to and marks the replication origin throughout the cell cycle. Licensing of the DNA replication origin starts when the critical cell division cycle protein Cdc6p binds to ORC. Cdc6p binding activates an ATPase switch in ORC. This activation causes an extended pre-replication complex (pre-RC)-like nuclease protection footprint on origin DNA. Our preliminary EM work reveals a ring-like structural feature in the ORC-Cdc6p complex that is similar in size to the replicative hexameric MCM helicase. This result supports the emerging concept that the helicase is loaded by replication initiators in a mechanism similar to the loading of the DNA polymerase clamp PCNA by the RF-C clamp loader complex. The formation of the extended pre-RC-like footprint by ORC and Cdc6p, a crucial event in replication origin licensing, is ATP-binding and -hydrolysis dependent.

This work is in collaboration with Dr. Bruce Stillman, the president and CEO of Cold Spring Harbor Laboratory. The Stillman lab performs molecular biology and biochemical portion of the work, and my lab carries out the cryo-EM and image processing and structural reconstruction.

Building upon our previous study on this system, our goals during the past year were to (1) further define the molecular organization of the ORC, and (2) investigate the conformational changes of ORC-Cdc6 upon ATP binding and hydrolysis events that underlie the DNA melting and helicase loading process.

TECHNICAL PROGRESS AND RESULTS:

During the past year, we have completed our goal of defining the ORC organization. The detailed ORC architecture suggested potential modes of interaction with DNA origins. A paper describing our EM study has been published this year [The architecture of the DNA replication origin recognition complex in *Saccharomyces cerevisiae*. Chen, Z., Speck, C., Wendel, P., Tang, C., Stillman, B., Li, H., Proc. Natl. Acad. Sci. USA 105(30): 10326-10331 (2008).]

We have also significantly improved the structure of the ORC by extensive electron microscopy and image processing of a much larger data set. We have obtained a cryo-EM map of ORC in complex with the replication origin DNA that is 66 base pairs in length. These studies provide insights into the molecular events at the initiation stage of the cellular chromosomal replication.

To expand this LDRD-supported work on the protein complexes of ORC and ORC-Cdc6, we proposed to study the interaction of these two protein complexes with the replication origin DNA. The proposal entitled "The Structural Basis of Eukaryotic Replication Origin Licensing by Cryo-EM" is now funded by NIH as a 5-year R01 grant, and this LDRD competed.

Diversification of Isoflavonoid Biosynthesis

LDRD Project 06-061

Chang-Jun Liu

PURPOSE:

Plant phenolics play vital roles in plant structure and plant defense responses. Isoflavonoids, as a large subfamily of soluble polyphenolics, are major anti-microbial phytoalexins in plant-pathogen interactions, and signal molecules mediating plant-microbial symbioses for N₂ fixation or Pi absorption. In addition, isoflavonoids constitute a group of phytoestrogens with potential dietary utility in chemoprevention of several lines of human diseases. Diverse biological activities of isoflavonoids lie on their characteristic chemical structures. The goal of this project is to characterize the key biosynthetic enzymes responsible for phenolic and polyphenolic formation and modification; to explore the structure and function of the key enzymes in the biosynthesis pathways, and to diversify isoflavonoid biosynthesis through laboratory protein evolution.

APPROACH:

We are applying biochemical genomics to functionally characterize isoflavonoid biosynthetic enzymes responsible for *O*-methyl- and *O*-acylation; X-ray crystallographic structural biology and protein mutagenesis/engineering approaches to explore the structure-function relationship of the key enzymes and to create novel functional enzyme variants.

TECHNICAL PROGRESS AND RESULTS:

In previous fiscal years (FY 2006 and FY 2007), we determined several sets of crystal structures of a *Medicago truncatula* *O*-methyltransferase in complex with different substrates, and we analyzed the unique structural features of the crystallized isoflavone *O*-methyltransferase. We revealed two substrate/product binding sites on the enzyme surface, in addition to the active site catalytic pocket of protein, and we created sets of enzyme variants in order to probe their regio-specific methylation and surface binding of the substrates. Structure-guided mutagenesis demonstrated that retaining such surface binding sites is critical for isoflavone substrate turnover.

During FY 2008 (half year of funding), we summarized our data for publication. Subsequently, according to the reviewers' comments, we further performed detailed biochemical analysis on the observed ligand-surface binding property of the enzyme. The studies include the kinetic determination for both the wild type and mutant enzymes; the fluorescence titration to assess the ligand-surface binding property; and the verification of enzyme conformational changes in the solution. The observation of isoflavone-enzyme surface interactions suggests a biochemical and structural mechanism adopted by natural product biosynthetic enzymes for trapping low concentrations of substrate *in vivo*.

In previous fiscal years (FY 2006 and FY 2007), we also identified a number of putative acyltransferases for flavonoid/isoflavonoid and anthocyanin modification from model legume *Medicago truncatula*. We over-expressed the identified malonyltransferase gene in the previously engineered *Arabidopsis* line. The overexpression led to the formation of the malonylated isoflavone products. During FY 2008, we performed metabolic profiling analysis on the created *Arabidopsis* transgenic plants harboring malonyltransferase. We further applied the

confocal microscopic imaging techniques to explore the unique subcellular localization of the identified malonyltransferases. We finally refined our results and successfully published them in the high profile journal, *Plant Journal*. By characterizing those (iso)flavone malonyltransferases, our studies provided useful molecular tools for manipulating plant natural product biosynthesis for promoting plant disease resistance, preventing plant biomass yield and for the production of the value-added bioactive metabolites.

In addition, we continually analyzed the other two novel *M. truncatula* acetyltransferases responsible for the structural modification of flavonoids. We determined their substrate specificity and the catalytic properties in detail.

During FY 2008, we also isolated two poplar lignin *O*-methyltransferase homologs, and we developed a simple colorimetric enzyme assay procedure to evaluate those phenolic *O*-methyltransferase activities. Together with the collection of other plant methyltransferases, we re-evaluated the substrate specificity for polyphenolics and phenolics and initiated the rational-designed protein evolution in order to create novel enzyme mutants to change their positional-specific methylation properties.

The structure-function studies on phenolic *O*-methyltransferases that were supported by this LDRD eventually led to obtaining a grant from DOE-BES for protein engineering of *O*-methyltransferases to probe lignin polymerization.

Development of a Cloud Condensation Nucleus Separator

LDRD Project 06-071

Jian Wang

PURPOSE:

The technical objective of this project is to develop a novel Cloud Condensation Nucleus Separator (CCN separator) that is capable of separating CCN and non-CCN at climatically important supersaturations. Once the CCN and non-CCN are separated, their microphysical, chemical, and optical properties can be further analyzed using a variety of aerosol instruments. Detailed studies can be carried out on what type of aerosols and how those aerosols affect the properties of clouds, which will lead to an improved understanding of the aerosol indirect effect on global climate. The development of the CCN separator supports the laboratory strategic research initiative of Aerosol Research, and is closely related to the Atmospheric Science Program of DOE. Given its unique capability, the CCN separator would likely be deployed in field studies with aerosol instruments from other research institutions, and be able to attract follow on research support from agencies besides DOE.

APPROACH:

Atmospheric aerosols could strongly influence the climate by scattering and absorbing sunlight (direct effect) and by changing the microphysical structure, lifetime, and amount of clouds (indirect effect). Among the effects of aerosol on climate, the indirect effects of aerosol are the most uncertain components in climate systems. Successful prediction of aerosol effects on climate requires a detailed understanding of the aerosol indirect effects, i.e. what type of aerosols and how those aerosols affect cloud properties. Among aerosol particles, only those that can grow into cloud droplets at certain supersaturations, which are also called cloud condensation nucleus (CCN), affect the cloud properties. Whether a particle can serve as a CCN under particular supersaturations depends on its physical size, chemical composition, water solubility, and surface property, etc. Detailed understanding of aerosol indirect effects necessitates

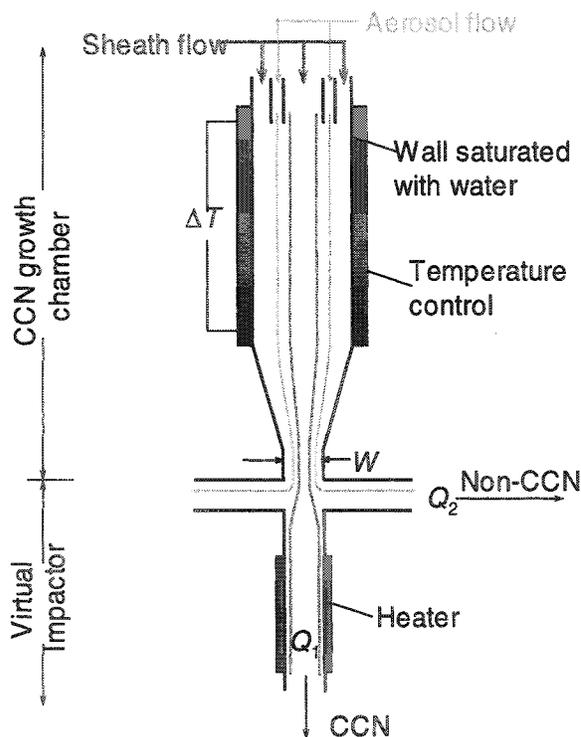


Figure 1. Schematic of the CCN separator.

characterizing the physical and chemical properties of CCN in different air masses and under a variety of meteorological conditions. Such studies are very rare, mainly due to the lack of a method for separating the CCN from the rest of aerosol particles (Non-CCN).

The proposed CCN separator is capable of separating CCN and non-CCN under climatically important supersaturations. The schematic of the CCN separator is given in Figure 1. The CCN separator consists of two major components. The first component is a CCN growth chamber that grows CCN into supermicron droplets under a prescribed supersaturation. The growth chamber is a cylindrical column, and its inner wall is made of porous ceramic that is maintained wet with water. Precise temperature controls are applied to generate a linear temperature gradient along the axial direction of the column. Due to the differences in water vapor diffusivity and air thermal diffusivity, a constant supersaturation is achieved near the centerline of the column. A wide range of supersaturations can be achieved by varying the flow rate, and the temperature gradient. The aerosol sample is introduced from the top of the column, and is confined in an annulus region sandwiched by particle-free sheath flows. Exposed to the supersaturation environment, CCN will grow into supermicron droplets at the end of the growth chamber. The grown droplets, along with non-CCN that remain unactivated, are then accelerated out of the chamber in a jet flow through a focusing nozzle. The second component, a Virtual Impactor (VI), separates the grown droplets and non-CCN by taking advantage of the substantial differences in their inertia. Non-CCNs, which are small and have little inertia, follows the gas flow streamline and exit from the sides (Q_2 Fig. 1). In contrast, supermicron droplets that are activated from CCN have enough inertia to cross the flow streamlines and be collected by the flow Q_1 (Fig.1). After separation, the CCN and non-CCN can be subsequently characterized using a suite of aerosol instruments.

TECHNICAL PROGRESS AND RESULTS:

We have carried out detailed simulations of the Cloud Condensation Nucleus (CCN) separator. Based on the simulation results, we have designed a CCN Separator that consists of a CCN growth chamber and a Virtual Impactor. The CCN separator is capable of separating CCN from non-CCN at supersaturations as low as 0.1%. The operating parameters, including flow rate and temperature settings, are optimized. The operating flow rate of the CCN separator increases accordingly with increasing supersaturation. At lower supersaturations, a lower flow rate is used to increase the residence time of the particles within the growth chamber, which allows CCNs to grow into sufficient large sizes and be separated. At high supersaturations, droplets grow faster, and operating at higher flow rate increases the sample rate and statistics of further characterizations.

Nanoparticle Labeled Neural Stem Cell Tracking *in vivo* by Magnetic Resonance Microscopy

LDRD Project 06-092

H. Benveniste, M. Maletic-Savatic, S. Wong, E. Chen and S. David Smith

PURPOSE:

The objective of this proposal is to develop and implement new technology to track the fate of neuronal (progenitor) stem cells (NSC) on a bio-systems level *in vivo* using (a) stem cells and nanoparticles coated with organic moieties (for tracking of exogenous stem cells) in combination with MR imaging and (b) non-invasive MR spectroscopy and metabolomics for tracking of endogenous stem cells.

APPROACH:

Over the past several years, attempts have been made to generate nanoparticles, such as superparamagnetic iron oxide (SPIO), that, when internalized by NSC *in vitro*, can be used for NSC tracking in the live brain using MR microscopy. NSC internalization of SPIO does pose some toxicity to the cells and clearance of the SPIO particles is extremely slow. In collaboration with the BNL CFN (Dr. Stan Wong), we have, therefore, investigated new particle approaches to label NSC using an alternative coating materials. Another approach for tracking of NSC which we have investigated, in collaboration with Dr. Maletic-Savatic and her team at SBU, is to use proton nuclear magnetic resonance (1H-MRS) and metabolomic profiling of NSC as a means of tracking them in the live brain.

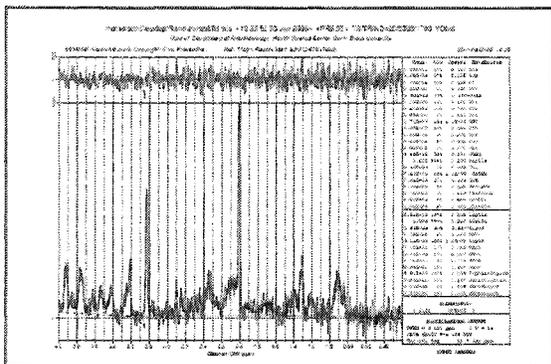
TECHNICAL PROGRESS AND RESULTS:

Progress in FY 2007-2008:

Nanoparticle Experiments: We have been working with Dr. S. Wong's team to optimize nanoparticle size and coating for uptake in to neural stem cells as well as defining the magnetic MR contrast signature of the phagocytized nanoparticles *in vivo*. Initially, we focused on magnetite nanoparticles and started testing magnetite nanoparticles in sizes from 5.6nm to 22 nm. These particles were adversely affecting the neural stem cells as previously reported (cf. 2007 LDRD progress report). Based on these data, we changed the coating of the stem cells; the new particles are rhodamine conjugated. Our initial toxicity experiments with the new nanoparticles have demonstrated favorable toxicity profiles, i.e. trypan-blue staining of the loaded neurospheres demonstrated that the cells were healthy and alive so loading did not kill them. We are in the process of investigating the effect of these new particles on neural stem cell differentiation.

MicroMRI Experiments: One of the major scientific objections to our approach to neural stem cell tracking in the live brain using non-invasive ¹H MRS, has been our analysis approach using singular value decomposition (SVD) software. This approach is based on the following: i) it is a non-fourier method of spectrum analysis; ii) it models the signal as a sum of exponentially decaying sine waves - Lorentzian lines in frequency domain; iii) it models noise as randomly distributed and iiiii) matrix diagonalization is used to determine the amplitude, frequency, decay rate of the spectral peaks of interest. Hoch et al. (1) correctly pointed out that Lorentzian lines are prone to false positives due to local magnetic field inhomogeneities, especially when performing experiments at high magnetic field. Additionally, the SVD software is partly iterative and requires user 'adjustments'. An alternate spectrum analysis software which is non-

iterative is commercially available – so called Linear Composition Modeling (LCModel) software. We have acquired this software and implemented it in our NSC experiments in the live rodent brain. We embarked on a series of new *in vivo* studies in rats to demonstrate that the biomarker enriched in neural stem cells at a frequency of 1.28ppm could be tracked in the live brain using LCModel software. Figure 1 shows a typical LCModel data output from the live rat hippocampus.



The 1.28ppm metabolite is referred to as 'Lip13a+Lip13b' in LCModel and is given in the column on the left hand side.

Figure 1. LCModel data format from an *in vivo* experiment of the rat hippocampus. The 1H MRS spectrum is visualized with the imposed model fitting and the 'residual' peak trace is depicted above. The quantitative metabolite information including the Cramer-Rao-Lower-Bounds are listed in the column on the left.

Figure 2 shows the biomarker Lip13a+Lip13b data from the live rat hippocampus derived from LCModel software before and after the rats were exposed to electroconvulsive shock (ECS). As can be seen in the eight rats there is a clear (and statistically significant) trend for an increase in the biomarker following ECS in agreement with our previous data published in science. Thus we have reproduced our data using alternative software.

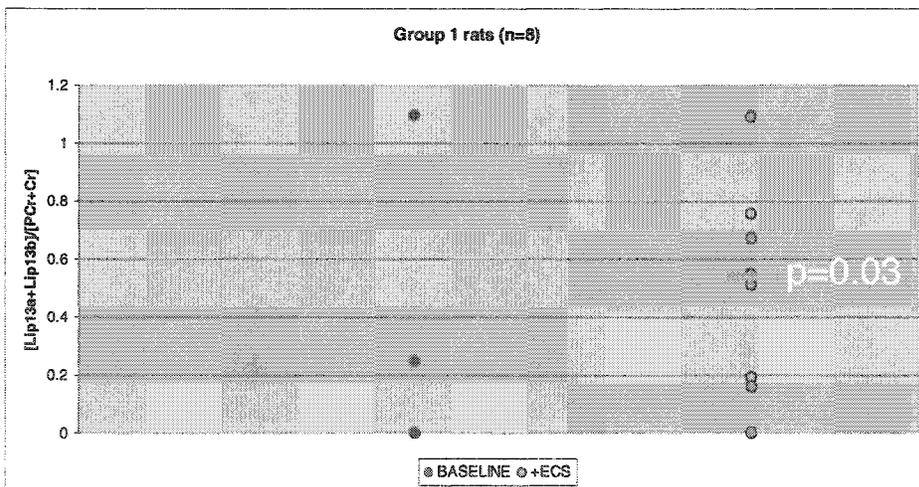


Figure 2. LCModel derived data: Lip13a+Lip13b analysis in the hippocampus of rats before and after exposure to electroconvulsive shock. As can be observed the data demonstrates a statistically significant increase in the metabolite after ECS in agreement with our previously published data.

1. Hoch JC, Maciejewski MW, Gryk MR. Comment on "magnetic resonance spectroscopy identifies neural progenitor cells in the live human brain". Science 2008;321:640; author reply.

MicroCT Methods of Quantitative Adipose Imaging: Development of a Long-Term Assessment Technique for Studying Obesity in a Rodent Model

LDRD Project 06-094

Gene-Jack Wang, A. Dilmanian, V. Boronikolas, M. Michaelides, P. Thanos, and Z. Zhong

PURPOSE:

Obesity is a major medical problem in the U.S. Because rodents are the most common animal models used in obesity research, accurate and precise measuring of body fat in rodents, particularly mice, has become a major challenge in this field. MicroCT (μ CT) is an excellent tool for this purpose because at low beam-energies it produces large differential image contrast between fat and lean tissue, allowing their separate quantification at fine reproducibility. In this regard an energy range such as 20-25 keV available from μ CT systems is ideal for imaging mice. Furthermore, the exquisite spatial resolution of μ CT in the three-dimensional CT-reconstructed images minimizes the so-called "partial volume effects" that otherwise limit the method's precision. Our μ CT system, SkyScan Model 1076, had a 20-100 kVp range of high voltage values, which, together with its different beam filtration options provided 20- to 70-keV mean spectral energies. It also had a fine spatial resolution, with pixel sizes of 9-, 18-, and 35- μ m. We used the energy-selective method of single-energy quantitative CT (SEQCT) to measure total body fat, together with some high energy images to correct for the lungs.

APPROACH:

The system employed cone-beam geometry, a micro focus x-ray tube and a horizontal bed. It was operated at 35- μ m pixel size, which produced a spatial resolution of \sim 60 μ m full-width-half-max (FWHM) in the CT reconstructed images. Our method, SEQCT, was used at 41-kVp, and with 0.5 mm Al beam filtration to produce a mean beam energy of \sim 24 keV. The resulting fat-to-lean tissue contrast was 0.58:1.0. We also used a high-energy beam, 100 kVp with 0.25 mm Cu beam filtration (70 keV mean energy) to better differentiate between lung tissue and fat. The analysis of the images included the following steps. First, the projection data were reconstructed to produce whole-body transaxial CT images. Examples of these CT images for a lean and an obese mouse are given in Figs. 1 and 2. Second, the values of the voxels in the CT data set, i.e., the attenuation coefficients of the tissues, were used to produce histograms of the voxel values (Fig. 3). These histograms clearly separated the fat voxels from the lean ones everywhere in the body of the mouse except for the lung region where the spectra of the attenuation coefficients for fat and lungs partially overlapped. Next, a) the counts of the total body fat were obtained by setting the limits on the histogram spectrum on the fat region and counting all voxels falling between the two limits, b) the total count of the lung voxels was then obtained by setting the voxel selection limits over the lungs and integrating the counts in the chest area, c) the lungs' voxel count was then subtracted from the total body fat count, and d) the resulting net fat voxel count was converted to grams of fat using a reference fat phantom with a known amount of fat in it. The measurements typically took about 40 min and the absorbed dose to the animal was 0.3 Gy.

TECHNICAL PROGRESS AND RESULTS:

We first obtained a 0.4% precision in measurements in repeated chicken-fat phantom studies. Next, we used three mice, 6-week old male C57, to compare the absolute value of the total body fat measured with our technique to that measured by the Bruker's minispec Lean/Fat Analyzer at Columbia University. The precision (reproducibility) of the total body fat measurement (standard deviation divided by the mean value) obtained from repeated studies with the chicken-fat

phantom was 0.36%, which we consider excellent. The pieces of the fat in the saline solution were moved around between measurements, and the bottle was repositioned in the system, to produce an independent CT image each time. This degree of precision would be invaluable for applying the method to longitudinal studies.

Our studies with the obese mice produced a reproducibility of 1.9% for total body fat normalized to the animal's weight. This reproducibility also is remarkably good.

Finally, the average value of the total body fat in three mice measured with the above method was only 65% of that measured with the minispec at Columbia University 3 days earlier. This discrepancy seems to stem from two factors. First, the mice experienced weight loss (1.7 g in average; which was 5.8 % of their body weight) between the two measurements. Although a 5.8% correction was introduced in the minispec fat results to correct for this loss, the percent fat loss could have been larger than the percent weight loss. Second, the two methods do not measure the same quantity; SEQCT measures only solid fat while minispec measures fat in all its forms.

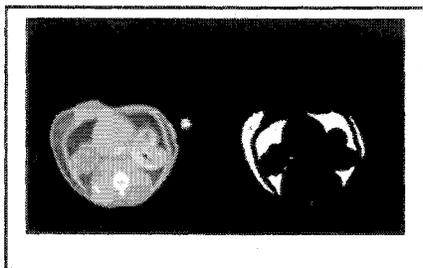


Fig. 1. A lean mouse abdomen with its fat regions highlighted.

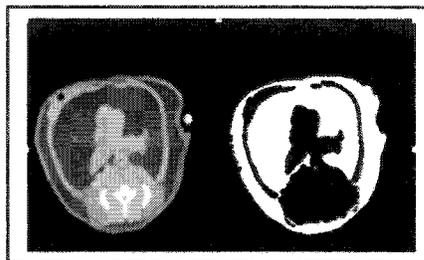


Fig. 2. As in Fig. 1 except for an obese mouse.

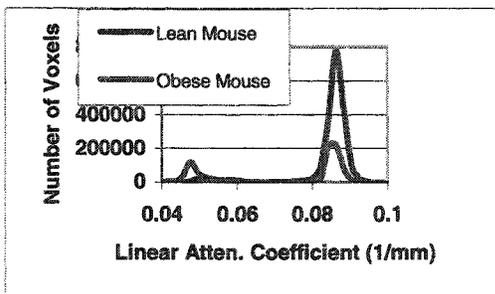


Fig. 3. Whole body histograms of CT voxel values.

SPECIFIC ACCOMPLISHMENTS:

The 0.36% reproducibility of the total body fat in chicken-fat phantoms obtained with SEQCT suggests that it is ideal for measuring total body fat in mice, particularly for longitudinal studies. The mice tolerate the radiation dose of ~0.3 without ill effects. The histogram method provides regional attenuation coefficient profiles of fat at high signal-to-noise ratio, which are valuable. The method is rich in information on the quality of the fat, and can be applied to small body regions with an adequate signal-to-noise ratio. In particular, we observed that the fat peak in the obese mice histogram shifts towards lower attenuation coefficients compared to lean mice (left peaks in Fig. 3). Because in fat cells the cytoplasm's attenuation coefficient is smaller than that of the cell nucleus, and because growth of the fat cell is only in its cytoplasm and not in its nucleus, the method allows calculating the relative fat cell size in different stages of obesity, which could be another useful piece of information.

Photocatalytic Reduction of CO₂ in Supercritical CO₂

LDRD Project 06-097

David C. Grills

PURPOSE:

The goal of this project is to determine if the photocatalytic reduction of CO₂ into useful chemicals and fuels can be achieved more efficiently than current state-of-the-art methods. With the ever-increasing costs of energy and the rapid depletion of the world's fossil fuel supplies, there is an urgent need for new technologies that will make use of renewable energy sources such as solar energy. The conversion of the abundant molecule, CO₂ into useful fuels and chemicals with solar-driven photocatalysts is thus an attractive prospect. We propose to employ supercritical CO₂ (scCO₂) as both the reaction medium and primary reactant for this type of process. This is an innovative approach since it eliminates the need for toxic organic solvents and may lead to many potential advantages, such as significantly higher reaction rates and catalyst turnover frequencies. The ultimate aim is to develop new, more efficient photocatalysts that are tailor-made for use in scCO₂.

APPROACH:

Supercritical fluids are a curious hybrid of gases and liquids. The use of scCO₂ (CO₂ at pressures and temperatures exceeding 1070 psi and 31 °C, respectively) as a replacement for conventional solvents in chemical processes has become increasingly common in the last two decades. However, its combined use as a solvent/reactant has received much less attention. The tunable physical properties of scCO₂ (e.g. density, viscosity *etc.*) and the fact that extremely high concentrations of CO₂ can be achieved (~20 M @ 3000 psi/35 °C) offers the possibility of dramatic enhancements in catalyst efficiency for the photoreduction of CO₂.

Various different transition-metal complexes have been investigated as potential photocatalysts for the reduction of CO₂, due to their long-lived charge-separated photoexcited states. A major setback however, has been that solvent molecules, such as DMF, THF, and CH₃CN, tend to coordinate to vacant sites at the metal center in the active catalytic species, and thus compete with CO₂ reactant molecules, substantially reducing the catalytic activity. Our approach therefore, is to completely eliminate the use of conventional solvents by replacing them with scCO₂, leaving CO₂ as the only available reactant to bind with the catalyst's metal center.

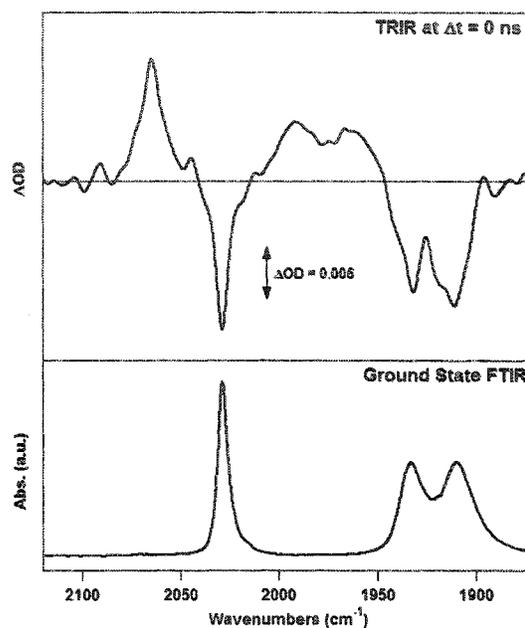
This project involves chemical synthesis to structurally modify a family of Re(α -diimine)(CO)₃L photocatalysts in order to render them soluble in scCO₂. This is necessary because scCO₂ is a relatively poor solvent, similar in solvating power to hydrocarbons such as hexane. Upon irradiation, this type of catalyst is known to reduce CO₂ to CO in the presence of a sacrificial electron donor such as triethanolamine. The photochemical and photophysical properties of our new catalysts are studied in conventional solvents and subsequently in scCO₂. This involves the use of fast time-resolved spectroscopic techniques (UV-vis and IR) on the nanosecond timescale to probe and characterize the intermediate species generated during photocatalysis. Catalyst efficiencies are determined by steady-state irradiation studies with GC and UV-vis detection.

TECHNICAL PROGRESS AND RESULTS:

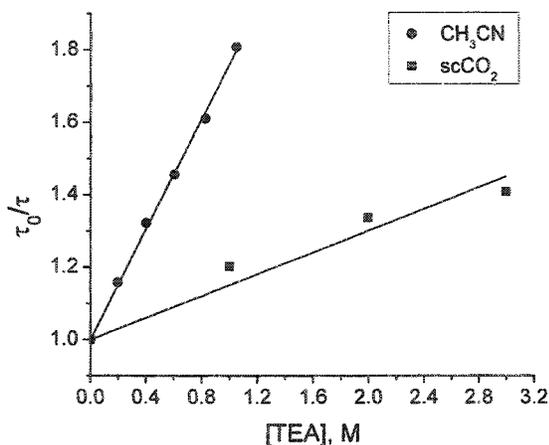
We previously synthesized two potential CO₂ photoreduction catalysts that are reasonably soluble in scCO₂. These were the dinuclear compound, [Re(CO)₃(dnb)]₂ (dnb = 4,4'-dinonyl-2,2'-

bipyridine), and the mononuclear $\text{ReCl}(\text{CO})_3(\text{dnb})$. Both of these molecules possess long nonyl alkyl chains attached to the bipyridyl rings, which rendered the catalysts soluble in both *n*-hexane and scCO_2 . The photophysical properties of these complexes were also investigated in both of these solvents. However, although these compounds were soluble in scCO_2 , and they exhibited suitable photophysical properties, it was expected that catalysts with a much higher solubility would be far more effective for CO_2 reduction.

We have therefore synthesized two new rhenium bipyridine complexes bearing polyfluorinated alkyl substituents. Such substituents are well-known to dramatically increase the solubility of otherwise insoluble metal complexes in scCO_2 . Two such catalysts were synthesized; $\text{ReCl}(\text{CO})_3(\text{dnb-F}_{26})$, **1a** and $\text{ReCl}(\text{CO})_3(\text{dub-F}_{34})$, **1b** (dnb-F₂₆ = 4,4'-(C₆F₁₃CH₂CH₂CH₂)₂-2,2'-bipyridine; dub-F₃₄ = 4,4'-(C₈F₁₇CH₂CH₂CH₂)₂-2,2'-bipyridine). The polyfluorinated tails did indeed enhance the solubility of the catalysts in scCO_2 , with dissolution in scCO_2 ($T = 35^\circ\text{C}$, $p = 2000$ psi) resulting in intense yellow solutions. UV-vis transient absorption spectroscopy of **1a** in scCO_2 after pulsed 410 nm laser excitation produced a spectrum with transient absorption bands at 370 and 470 nm. These bands, which together decayed with a lifetime of 34 ns, are characteristic of the desired metal-to-ligand charge transfer (MLCT) excited state. Time-resolved infrared (TRIR) spectra of **1a** in scCO_2 solution, formed after 410 nm laser excitation (see right), exhibited three new ν_{CO} bands at 2066, 1990 and 1956 cm^{-1} , which are also highly characteristic of an MLCT excited state.



In order for **1a** and **1b** to act as effective photochemical CO_2 reduction catalysts, their MLCT excited states must be efficiently quenched in the presence of a suitable electron donor. Therefore, we determined quenching rate constants with triethylamine (TEA) by carrying out



emission lifetime measurements in CH_3CN and scCO_2 as a function of [TEA]. The resulting Stern-Volmer plots (shown left for **1a**) revealed quenching rate constants, k_q of $2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in CH_3CN and $4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in scCO_2 . Given the much lower polarity of scCO_2 relative to CH_3CN , this relatively small difference in k_q is quite remarkable. These results indicate that **1a** and **1b** are excellent candidates as catalysts for the photochemical reduction of CO_2 to CO in scCO_2 . Photocatalysis experiments with these complexes are currently in progress, and our preliminary data show the formation of CO in both DMF and scCO_2 .

Detailed results, including turnover numbers and kinetic studies, will be reported soon.

QCD Thermodynamics at Non-Zero Temperature and Density

LDRD Project 07-001

Frithjof Karsch

PURPOSE:

The objective of the project is to improve our understanding of the QCD phase diagram through a systematic study of phase transitions in an extended parameter space defined by the quark mass, the temperature and the baryon chemical potential. The aim is to reach better control over the baryon density or chemical potential dependence of the QCD transition and improve current studies of the chiral critical point in the QCD phase diagram. The project provides important input to the preparation of experimental programs (low energy runs at RHIC and the CBM experiment at FAIR) that aim at a study of QCD at high baryon number density.

APPROACH:

It is expected that the QCD phase diagram changes qualitatively when going from vanishing baryon chemical potential to values of the order of a few hundred MeV. Model calculations suggest that a line of first order phase transitions emerges at non-zero baryon chemical potential starting at a critical point (2nd order phase transition point). Similarly the transition changes from a continuous crossover to a first order phase transition when the quark mass is reduced to sufficiently small values. We use Taylor expansion techniques to analyze the phase diagram of QCD and study the connection between transitions that exist at small quark masses and those conjectured to exist at non-zero quark chemical potential. For this purpose we developed a program that automates the calculation of higher order Taylor expansion coefficients. This allows the performance of calculations at higher orders in the expansion and will improve our knowledge of finite density QCD considerably.

The numerical calculations are performed in the context of studies of QCD Thermodynamics performed by the RIKEN/BNL-Bielefeld-Columbia Collaboration on the QCDOC and BG/L computers at BNL as well as on the apeNEXT computer at Bielefeld University, Germany. The collaboration involves about 15 members from Bielefeld University (Prof. E. Laermann et al.), Columbia University (Prof. N.H. Christ, Prof. R.D. Mawhinney, M. Cheng) and members of our BNL based Lattice Group (S. Ejiri, P. Petreczky, C. Miao, C. Schmidt, W. Soeldner and myself). S. Ejiri also participates in the WHOT collaboration, which performs studies of finite temperature and density QCD with so-called Wilson fermions.

TECHNICAL PROGRESS AND RESULTS:

During most of FY2008 we have performed calculations of Taylor expansion coefficients up to 6th order. This gave us new insight into fluctuations of baryon number, electric charge and strangeness at high temperature. We could show that the higher moments of these fluctuations of conserved charges show clear deviations from a simple resonance gas picture at low temperature. Moreover, we found clear evidence that already at about twice the transition temperature quarks are the dominant degrees of freedom that carry these conserved charges. Through a systematic study of the quark mass dependence of various thermodynamic quantities we got a first insight into the influence of light Goldstone modes on the thermodynamics in the chiral limit.

We performed these studies mainly with improved staggered fermions. However, some studies also have been performed with improved Wilson fermions. First exploratory studies have also

been performed within a chiral fermion formulation (domain wall fermions). This will in the future allow better control over the influence of chiral symmetry restoration on the deconfining properties of the QCD phase transition.

SPECIFIC ACCOMPLISHMENTS:

This project resulted in two publications in Physical Review D, a publication in the European Physical Journal C and a publication submitted to Physical Review D. They present new results on the density dependence of the QCD equation of state, the fluctuation of conserved charges and the structure of the QCD phase diagram. These results have been reported at several conferences, including this year's lattice conference and the Quark Matter conference. They are published or are going to be published in six conference reports.

Lattice QCD Simulations on BlueGene/L

LDRD Project 07-002

Frithjof Karsch

PURPOSE:

The objective of the project is to build up a computational environment with highly optimized programs and libraries that allows the performance of efficient QCD thermodynamics simulations on BG/L computers. This requires to port the Columbia Physics System (CPS) software package, which forms the basis for the comfortable computing environment used on the RIKEN/BNL and DOE owned QCDOC computers, also to BlueGene/L. CPS will be used to run efficiently QCD thermodynamics projects on BlueGene/L.

APPROACH:

The BlueGene/L architecture has many features in common with the QCDOC computers installed at BNL. The basic parallel computing paradigm thus can easily be mapped onto the BlueGene/L machines. However, on QCDOC central parts of the computing programs have been coded in Assembler to reach satisfactory efficiency. These parts of lattice QCD programs require an individual treatment on different computer architectures and need to be ported to BlueGene/L. Moreover, recent advances in lattice simulation and integration schemes (RHMC algorithm, Omelyan integration, quotient force terms) as well as the development of refined fermion discretization schemes with improved flavor symmetry (stout action, domain wall fermions) require the development of new programs. These have to be optimized for new computers such as BlueGene/L and have to be integrated into a common library environment, the CPS software package used by our BNL based Lattice Group (S. Ejiri, P. Petreczky, K. Huebner, C. Pica, C. Schmidt, W. Soeldner and myself) in the joint research projects with the lattice group at Columbia University as well as research groups at LLNL and LANL.

TECHNICAL PROGRESS AND RESULTS:

At the end of FY2007, our basic routines for efficient calculations on the BlueGene/L and P computers at the New York Center for Computational Science, which is hosted by BNL, have been fully functional. They have been used in our large-scale projects on QCD thermodynamics since then. New programs have been developed for studies of transport coefficients in pure gauge theories and the analysis of spectral functions on large lattices equilibrated in quenched QCD. Some additional work has been going on to utilize parallel I/O on the BlueGene/P.

The QCD thermodynamics project on BlueGene/L computers is to a large extent part of the so-called hotQCD Collaboration, a consortium of lattice gauge theory groups in the U.S. The goal of this collaboration is to extend existing studies of QCD thermodynamics by performing simulations with parameters that are even closer to the continuum limit. This will improve control over systematic errors in the continuum extrapolation and will improve results obtained for the QCD equation of state and transition temperature. Apart from this we started calculations of the equation of state with physical values of the light quark masses and a physical value of the strange quark mass and performed a first study of screening properties in the magnetic sector of QCD (spatial string tension). These projects are part of the RBC-Bielefeld research project, which also uses computing resources on the BNL QCDOC computers and the apeNEXT computer in Bielefeld.

SPECIFIC ACCOMPLISHMENTS:

This project resulted in three publications in *Physical Review D*. Results of this project have been reported at several conferences, including the Quark Matter conference in Jaipur, India, and the Lattice conference in Williamsburg, Virginia. These results are published or are going to be published in four conference reports.

Proof-of-Principle Laser System for ILC Positron Source

LDRD Project 07-004

Igor Pogorelsky

PURPOSE:

Inverse Compton scattering between counter-propagating laser- and electron-beams is one of the prime candidates for generating intense γ -rays for diverse applications, including a polarized positron source for future colliders such as the ILC and CLIC. Production of a high-current positron beam requires a multi-kHz picosecond laser of multi-kW average power that is far beyond present-day industry capabilities. We propose to circumvent this constraint capitalizing on the fact that the bulk of the γ -ray energy is consumed from the electron beam, while the attenuation of the laser is negligible. This provides the possibility to “recycle” laser energy for multiple Compton interactions thus relaxing the laser requirements. The goal of this project is to demonstrate the feasibility of this approach leading toward its broad application for lepton-lepton colliders and laser synchrotron light sources for multi-disciplinary needs.

APPROACH:

A precursor to this project was the ATF Compton scattering experiment, which demonstrated a record-high x-ray yield that satisfies the ILC requirements for a single laser/e-beam interaction. This success was based on the use of a mid-IR picosecond CO₂ gas laser that produces 10 times more photons per Joule of laser energy than shorter-wavelength solid-state lasers. Note, that a high-pressure (~10 atm) gas laser medium is required to provide the sufficient spectral bandwidth for picosecond pulse amplification. Up-scaling the x-ray (gamma) yield via multiple (up to 100) similar laser/e-beam interactions, while firing a laser just once, requires placing the laser/e-beam interaction point (IP) inside a regenerative laser ring cavity as is illustrated in Fig.1. Optical losses of a circulating laser pulse after each round-trip are compensated by a high-pressure CO₂ laser amplifier located within the cavity. The aforementioned energy recycling effectively brings a commercially available 0.5-kW high-pressure CO₂ laser to the required multi-kW level.

Development, simulation and experimental testing of such a regenerative CO₂ laser cavity constitute the major part of this project. Along with Igor Pogorelsky (PI, Scientist), the main contributors to this project are Vitaly Yakimenko (Scientist, Head of the ATF) and Mikhail Polyanskiy (Post-Doctoral Research Associate).

TECHNICAL PROGRESS AND RESULTS:

1st -Year Results

During the first year of the project (FY-2007), two milestones were accomplished:

The first was the experimental demonstration of the possibility of incorporating the ATF's basic Compton scattering optical setup (a pair of confocal, off-axis parabolic mirrors with a hole for transmitting the e-beam and γ -rays) into a regenerative laser cavity and circulating a train of picosecond laser pulses through the Compton IP; the second was the development of a core computer model of a regenerative picosecond CO₂ laser amplifier.

2nd -Year Results

During the second year of the project (FY-2008), the work progressed in both areas. Through experiments, we successfully injected a picosecond laser pulse into the amplifier cavity using an

optically controlled semiconductor switch. We now anticipate that this device will be part of the prototype cavity design. Simultaneously, we achieved higher energy (up to 300 mJ) in a pulse train circulating through the Compton IP. In order to control the uniformity of the train in the presence of the ATF's high-gain amplifier, we artificially introduced high optical losses. This results in fast damping of stored energy, and train truncation after ~ 20 passes.

To solve this problem, we added more sophistication to our computer model. The improved program provides not only detailed insight into the dynamics of the laser pulse evolution in the regenerative amplifier, but allows for optimization of the amplifier parameters, such as gas composition and characteristics of the electric discharge. One of the outcomes of this development was the conclusion to enrich the laser gas with CO_2 isotopes. Simulation results presented in Fig.2 and Fig.3 illustrate how the isotopes extend the pulse train and improve the time structure of individual pulses within the train. Simultaneously, isotopes provide a sufficient bandwidth to allow reducing the laser working pressure twice that offers a significant technological advantage.

Future Prospects and Milestones

We work on preparations to test a pulse-train with an isotopic CO_2 amplifier. The result of this test, along with computer modeling, will provide a platform for culminating this LDRD project with a practical design of a prototype laser system that meets the collider requirements.

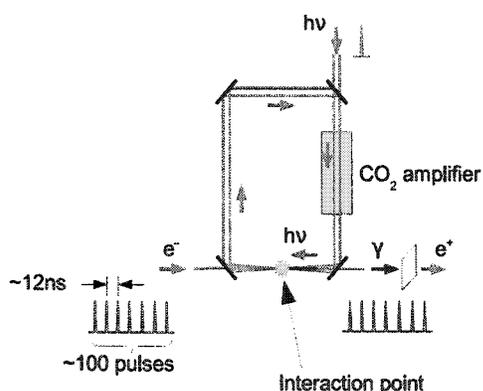


Figure 1. Principle diagram of intra-cavity, high-repetition Compton source.

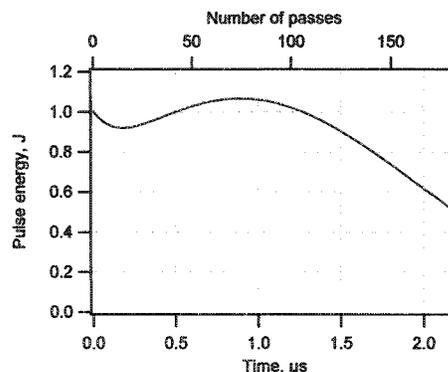


Figure 2. At properly chosen laser amplifier parameters and realistic optical losses (5% per pass) the pulse train can be stabilized at the 1 J level over 100 passes.

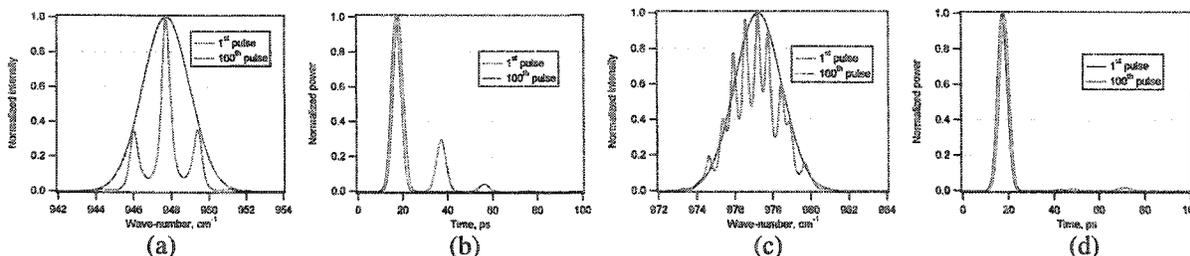


Figure 2. Spectral modulation of the pulse train by the laser amplifier and the corresponding time structure of individual pulses: (a) and (b) with a regular 10-atm laser gas composition, (c) and (d) with the 5-atm multi-isotope laser.

Sensitive Searches for CP-Violation in Hadronic Systems

LDRD Project 07-005

Yannis Semertzidis

PURPOSE:

To develop a sensitive storage ring electric dipole moment (EDM) experiment capable of probing the EDM of the deuteron and proton at the 10^{-29} e-cm level. At this level they will probe new physics at the 300-TeV mass scale, or if there is new physics at the LHC scale (~ 1 TeV), they will probe CP-violating phases at the 10^{-5} rad level, an unprecedented sensitivity level. If a non-zero EDM value is found, it will help explain the baryon asymmetry of our universe (BAU).

The experiment that will result from this development will be launched at the AGS experimental floor and will use BNL's capability and experience with high intensity polarized beams. The deuteron and proton EDMs will provide a new program (facility) of probing EDMs of charged particles directly. This current LDRD supported the development of accelerator techniques to achieve a spin coherence time of 10^3 s required to achieve the stated sensitivity.

APPROACH:

To develop the storage ring EDM method we needed to make progress in several parts of the experiment. One fundamental part is the spin coherence time (SCT) also known as polarization lifetime. We took two different approaches: 1) we studied this analytically (Professor Yuri Orlov from Cornell University, the world's expert on non-linear beam and spin dynamics (he invented most of this physics himself some 30 years ago), and 2) by simulation using state of the art computer simulations for particle and spin dynamics. The simulation program was written by Alfredo Luccio of CAD and we have hired Dr. Fanglei Lin (supported with this LDRD) who had experience with that program as part of her Ph.D. thesis work (studying spin resonances in the AGS). Dr. Lin was a student of S.Y. Lee of IUCF, a world renowned spin and beam dynamics physicist. Nikolai Malitsky of NSLS II is the author of the beam dynamics part of the program and essential to the success of this research. William Morse, the resident spokesman of the muon g-2 experiment, is also an essential member of the team.

The allocation of the resources is given bellow:

TECHNICAL PROGRESS AND RESULTS:

Dr. Fanglei Lin started with us in October 2007 and her current appointment ends September 2009.

She modified the program that was used for simulating polarized beam propagation in large size rings like e.g. RHIC, AGS, COSY (located at Julich in Germany) to make it more appropriate for smaller size rings. The issue at hand is the accuracy level that is needed. It turned out that we needed to expand the coefficients describing the beam motion up to 9th order for adequate accuracy.

Specifically, we need to store the particles in the EDM ring for about 10^3 s, which takes about 1 billion revolutions. The program was significantly modified to be able to accurately produce the beam dynamics for 10 million revolutions. The computer simulation takes about 30 minutes of computer CPU time for each particle.

Next we tested (tried to calibrate) the program by estimating the so called pitch correction in g-2 type of experimental setting. It turns out that the mode of operation of the program was not accurately enough to estimate this effect. Dr. Lin is currently implementing the spin tracking part of the program into the general program that estimates the beam dynamics part. This implementation should take another two to three months to finish.

In the process of estimating the pitch correction we found out that a classic paper describing this effect did not accurately describe it for storage rings with magnetic focusing systems. The paper was found to be correct for electric focusing systems (the muon g-2 experiment run with an electric focusing system and there is no problem there). We are preparing a paper describing the effect and the correction.

Dr. Lin has already used sextupole magnets in her storage ring lattice simulation to prolong the SCT of deuterons to about 10 s. We expect that when we have the complete program of beam and spin dynamics at the required accuracy we will be able to make good progress towards achieving the 10^3 s required for our experiment. Since the sensitivity goes as the square root of the SCT, there is a factor of 10 in sensitivity to be gained here.

For the current FY2009 (funded by the current LDRD) we expect to have the required accuracy for both beam and spin dynamics (we currently have the required accuracy for only the beam dynamics part of the program). We will also expect to achieve 50 s of SCT.

For the next fiscal year we expect to achieve the required 10^3 s of SCT for the success of the storage ring EDM experiment. Additionally, we expect to be able to simulate the very small systematic error effects and their cross interactions when they are tracked for $>10^2$ s. They will guide us in trying to understand how to minimize them and how the data will look like at the early stages of the experiment.

Dr. Lin has presented her work at major conferences and it has been included in the deuteron EDM proposal submitted to the BNL RHIC/AGS PAC and the R&D plan. The proposal has achieved scientific approval. We are currently in the R&D phase and we are scheduled to have a first technical review in the fall of 2009.

Feasibility and Design Studies for a Detector for e+p, e+A, p+p, p+A, and A+A Collisions at BNL

LDRD Project 07-006

Thomas Ullrich

PURPOSE:

A future Electron-Ion Collider (EIC) embodies the vision of the field of High Energy Nuclear Physics for reaching the next QCD frontier: the study of gluons which bind all atomic nuclei. An EIC, which provides high-luminosity collisions at centre-of-mass energies from 30-100 GeV with polarized electron and nuclear beams may be sited at either BNL (eRHIC) or JLAB (ELIC).

The aim of this LDRD project is two-fold. One goal is to strengthen the physics case for a future EIC by conducting studies that demonstrate the feasibility of a broad range of measurements with high physics impact. From these studies, requirements on the machine (beam energies and luminosities) and on detector design will evolve. The latter is the second goal of this project, which is to define the capabilities (acceptance and particle identification) a future detector must provide and then translate these requirements into a design for a realistic EIC detector. In order to achieve this, detailed physics simulations must be performed to optimize the design. The case of e+A physics is especially challenging in a collider environment, as it must allow for the detection and reconstruction of the scattered low-energy electron. In order to for a full study of all aspects of QCD, we intend to see if this multi-purpose detector can be designed in a way that it is also pertinent to the study of p+p and p+A collisions.

The outcome of this LDRD will provide a detector design that will serve as a baseline detector for the EIC, allowing for the study of e+p and e+A physics over a broad kinematic spectrum. These results will provide first input to the 2012 NSAC Long Range Plan, something that is essential for the future of the EIC project as a whole.

APPROACH:

The physics at an EIC is sufficiently different to that at RHIC that new detectors and approaches are required to understand the physics. Therefore, the generation of simulated e+p and e+A collisions are essential in order to identify this. By using existing e+p generators and detector proposals, we are able to make progress in understanding the requirements. Once this has been accomplished, we will move ahead and modify these generators to also work for e+A collisions, something that is essential especially in the case of diffractive physics.

TECHNICAL PROGRESS AND RESULTS:

In order to simulate e+A collisions, one approach, which is possible, is to produce e+p simulations and apply a MC Glauber wrapper (HIJET) to these data. Although there are no nuclear effects in HIJET (such as shadowing, EMC effect), this is a satisfactory first approach for inclusive DIS collisions but not so for diffractive collisions, where there should be significant differences between e+p and e+A. A diffractive event is one in which the virtual photon emitted from the electron interacts with a pomeron from the nucleon/nucleus, with, in the case of coherent diffraction, the nucleon/nucleus staying intact in the final state. As well as allowing for the study of the pomeron structure, diffractive collisions are particularly important as the cross-section for diffractive events is predicted to be proportional to the square of the gluon density. The gluon density is one of the principal measurements at an EIC as it will determine whether the

saturation regime has been reached. At HERA (e+p), diffractive events were found to contribute 15% of the total cross-section and in e+A collisions at an EIC, this may increase to up to 30-40%.

One of the technical challenges which exists is the ability to identify and tag diffractive events. In e+p collisions, this is possible in some cases through the measurement of the final-state proton in Roman Pot detectors far down the beam-line. In e+A collisions, however, another method has to be used. We have been investigating one approach whereby one can take advantage of the fact that in diffractive events, there is a large gap in rapidity between the most forward particle (MFP) produced in the event and the outgoing proton/nucleus. To study this, we have generated e+p events for a number of possible EIC energies, using the RAPGAP MC particle generator - a first step in this investigation because no e+A generator currently exists.

By generating both diffractive and inclusive DIS events, we were able to obtain the results depicted in Fig. 1, which shows the MFP distribution in both systems. A clear difference exists at all energies between the two distributions and, interestingly, this is also the case for the lowest energy of 2+100 GeV - a low-energy option which has been proposed in recent months as part of a staged approach to an EIC. Using these distributions, it is possible to calculate the value of rapidity where it is appropriate to place a cut in order to extract the data. This is shown in Fig. 2 which plots the efficiency and purity versus the rapidity, where the efficiency is the fraction of diffractive events measured and the purity the fraction of diffractive events out of all measured events. It is encouraging that, according to the simulations, it is possible to have > 90% efficiency and purity for all energies. The rapidity distributions also show that it is important to have a fully hermetic detector.

The next step in this analysis of diffractive events is to modify the RAPGAP MC generator so that it will generate e+A events as well as e+p events. This will be an important achievement as diffractive events in e+A and e+p collisions may have very different signatures. Complimentary to inclusive measurements, the physics of jet production will also provide information on the gluonic properties of the medium and their measurement will also be an important constraint on the design of a detector.

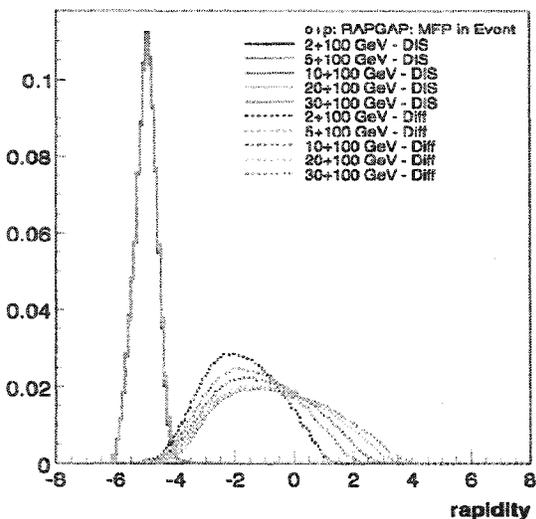


Figure 1: Most Forward Particle distributions for inclusive DIS and diffractive events

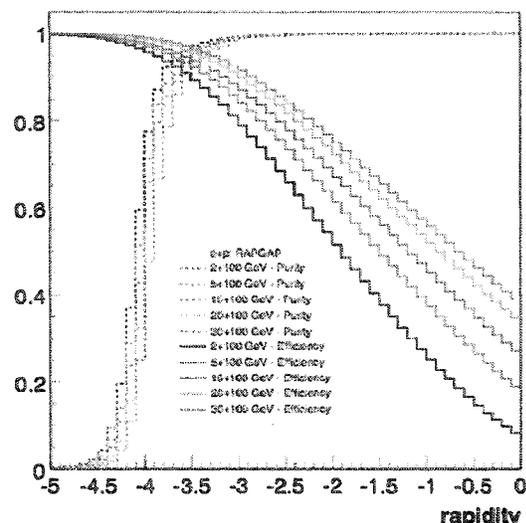


Figure 2: Efficiency and purity plotted versus energy for different EIC energies

A Novel and Compact Muon Telescope Detector for QCD Lab

LDRD Project 07-007

Zhangbu Xu

PURPOSE:

We propose an R&D research on a large-area and cost-effective muon telescope detector (MTD) for RHIC and for next generation detectors at future QCD Lab from state-of-art multi-gap resistive plate chamber (MRPC) with large module and long strips. Conventional muon detectors rely heavily on tracking stations while this new R&D project proposes to use good timing and coarse spatial resolutions to identify muons with momentum of a few GeV/c. This R&D project will focus on studying the capability of muon identification based on timing resolution from the MRPC detector with large module, long strips and fast electronics for online trigger. We have carried out timing resolution study at FermiLab test beam facility (T963), prototype in real environment at STAR in Au+Au, p+p and d+Au collisions and plan to install a new prototype equipped with the Time of Flight (TOF) electronics for p+p collisions at RHIC in run 2008-2009. This allows us to assess the detector time resolution, and its trigger and particle identification capability. A large-area muon detector around center of mass at RHIC will be crucial for advancing our knowledge of Quark-Gluon Plasma (QGP). It directly addresses many of the open questions and long-term goals proposed in 4 RHIC white papers published in Nuclear Physics A 757 (2005). Since muons do not participate in strong interactions, they provide penetrating probes to the strongly interacting Quark-Gluon Plasma.

APPROACH:

A compact detector identifying muons of momentum at a few GeV/c should achieve hadron rejection of a few hundreds and allow us to investigate dimuon pair from virtual (heavy) photon decays, QGP thermal radiation, possible correlations of quarks and gluons as resonances in QGP, initial lepton production, and heavy flavor (charm quark and bottom quark). In addition to an effective trigger and cleaner signal-to-background ratio, electron-muon correlation can be used to distinguish lepton pair production and heavy quark decays.

We propose an R&D research on a large-area and cost-effective muon telescope detector (MTD) for RHIC and for next generation detectors at future QCD Lab from state-of-art multi-gap resistive plate chamber (MRPC) with large module and long strips. Conventional muon detectors rely heavily on tracking stations while this new R&D project proposes to use good timing and coarse spatial resolutions to identify muons with momentum of a few GeV/c. Basic technology but with small pads has been proposed in STAR and PHENIX at RHIC and ALICE at Large Hadron Collider (LHC) as Time-of-Flight Detectors. This R&D project will focus on studying timing and spatial resolution from the MRPC detector with large module, long strips and fast electronics for online trigger to achieve necessary muon identification and hadron background rejection.

Components for the prototype and contributions from other collaborators:

1. *Long MRPC modules: Prof. Cheng Li, and Dr. Yongjie Sun (USTC/China), Prof. Yi Wang and Dr. Xiaobin Wang (Tsinghua University/China)*
2. *Front-end electronics and gas box: Drs. Bill Llope and Geary Eppley (Rice)*
3. *Trigger electronics and logics: Dr. Jack Engelage (UC Berkeley, Space Lab)*
4. *Simulations: Guoji Lin (Yale University)*

5. *T963 test beam: Dick Majka, Nikolai Simernov, Guoji Lin (Yale University), Yi Wang and Xiaobin Wang (Tsinghua Univeristy/China), Zhangbu Xu (BNL)*
6. *Prototype in STAR for 2007—2008 and data analysis: Lijuan Ruan and Patricia Fachini (BNL)*
7. *Test setup at BNL physics building: L.J. Ruan, X.B. Wang, and Z.B. Xu*

TECHNICAL PROGRESS AND RESULTS:

In the earlier years, we have successfully produced 4 Long MRPC modules in China. The results from cosmic ray and beam tests using prototype front-end electronics show good timing resolution (less than 70 ps), high efficiency (>95%) and good spatial resolution (<1cm). This satisfies the needs for a large-area muon detector. Modules installed behind the STAR magnet have successfully taken triggered data in Au+Au collisions, and offline tracking of particles from Time-Projection Chamber (TPC) is able to match with hits from Long MRPC. In the current fiscal year:

1. With the run-by-run analysis on beam test data samples, the Long MRPC was found to have a consistent performance.
2. Modules installed behind the STAR magnet have successfully taken triggered data in d+Au and p+p collisions in year 2008, and offline tracking of particles from the TPC is able to match with hits from Long MRPC.
3. The offline analysis indicates that the hits from the modules matched with TPC tracks have two components: muons and hadrons. Muons results in a narrow Gaussian spatial distribution, after traversing the magnet steel; while hadrons result in a much broader distribution. This feature is consistent with simulation. The muon-to-hadron ratio was found to be ~1.7 with tracking matching only. Additional dE/dx and time of flight cuts significantly enhanced the muon-to-hadron ratio.
4. Among the muon component, primary muons was found to be about 6-10%; secondary muons from pions was found to be about 30-40% while others are dominated by kaon decay.

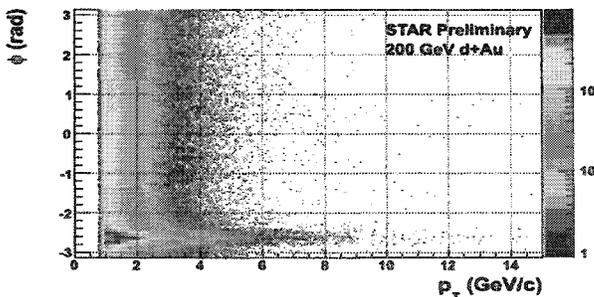


Fig.1 Azimuthal angle distribution of particles from STAR TPC in d+Au collisions versus transverse momentum p_T . The peak shows an enhancement of particles yields at the angle where MTD is positioned

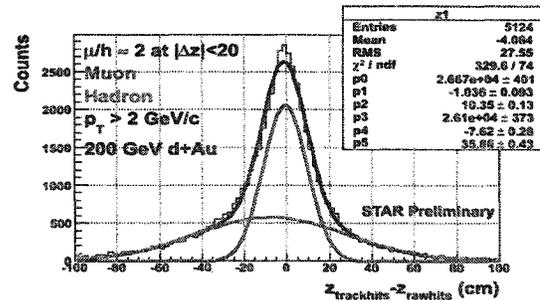


Fig.2 The difference of the two position values in the z direction (Δz), one measured from Long MRPC and the other extrapolated from TPC tracking. Two components were observed. A double Gaussian function was used to fit the distribution.

Future work and milestones:

1. Make a prototype MTD tray with new electronics (same as TOF) and install it at STAR
2. Obtain data in p+p collisions at STAR in 2008—2009 run
3. Assess time resolution, hadron rejection, and muon identification efficiency
4. Optimize the detector configuration and electronics
5. Proposal for full-coverage muon telescope detector for STAR

Design Optimization of a Reactor Neutrino Experiment

LDRD Project 07-010

David E. Jaffe, Steve Kettell and Laurence Littenberg

PURPOSE:

Use of Geant4-based simulation to evaluate and optimize proposed elements of the Daya Bay Reactor Neutrino Experiment including options for a muon veto system and tracker. A portion of the funding is to be used for simulation and software workshops (one per year).

APPROACH:

The Daya Bay experiment offered the opportunity for Brookhaven to become a leader in the reactor neutrino effort that strives to measure the currently unknown neutrino mixing parameter $\sin^2 2\theta_{13}$. The muon veto system is essential in order for the Daya Bay experiment to reach its design sensitivity. Careful evaluation and optimization is needed to ensure that the cosmogenic background can be sufficiently well-suppressed and that the remaining background can be reliably estimated. Extensive use of Geant4-based simulation, validated by comparison with relevant data, is employed to evaluate muon veto system designs and background estimations. Many of the studies have been done in collaboration with Hongshang (Kevin) Zhang, a postdoc hired with resources of this LDRD.

TECHNICAL PROGRESS AND RESULTS:

Design of the muon veto system provided in part by this LDRD lead to approval of the Daya Bay Reactor Neutrino Experiment following a January Technical Design Review (CD2/3a) and subsequent CD3b approval after June 2008.

Additional software was written and studies were performed, mainly by Kevin Zhang, to assess the implications of detailed final engineering designs for the muon veto system.

A week-long software workshop was held at BNL 7-11 April 2008 and attended by 34 collaborators of the Daya Bay Experiment. Travel, accommodations and per diem of ten of the attendees were fully or partially funded by funds from this LDRD. The workshop was deemed a success. Dozens of software tasks were identified and volunteers came forward to claim them. A significant fraction of the tasks have subsequently been completed or are actively being worked on. A detailed hierarchical documentation plan using e-mail archives, wiki and formal user mail was adopted and is in use and working well.

Following the decision of the Daya Bay collaboration to move to a new software framework ("Gaudi", developed by LHCb and in use by ATLAS, LHCb and numerous other experiments), a validation procedure was agreed upon to facilitate migration to the new framework. Kevin Zhang took the lead on the validation of the portion involving the muon system. After correction of many small problems and oversight, the simulation of the muon system was judged to be validated. Kevin Zhang's experience with the new framework was invaluable in assisting the validation of the simulation of the antineutrino detectors. The new framework is now in use by the entire collaboration.

Development of Laser Beam Shaper for Low Emittance Electron Beams

LDRD Project 07-019

Triveni Rao and Thomas Tsang

PURPOSE:

Typically photocathode drive laser output is characterized to be Gaussian in transverse and longitudinal dimensions. However, applications such as high brightness electron injectors require non Gaussian shapes to minimize the emittance of the electron beam. For example, high-current ERL, such as the one being built at BNL, requires flat-top transverse and longitudinal profile with pulse duration of ~60 ps for low charge (<1.4 nC) and ~120 ps for high charge (>5 nC) operations. This project is directed towards evaluating different techniques for modifying the beam profile, selecting the ones suitable for the ERL operation, and designing, constructing and testing the selected beam shaper.

APPROACH:

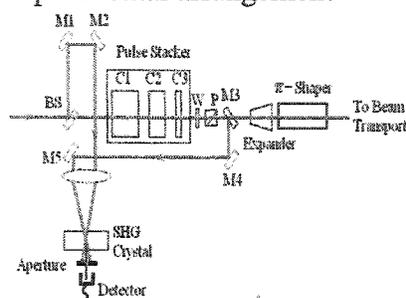
The laser pulse needs to be shaped in both the time (longitudinal) and the space (transverse) domains. The initial beam shaping is aimed to generate a rectangular beam profile. Although a number of techniques can be used to shape the laser beam, after evaluating various techniques theoretically and experimentally, a Gaussian-to-flat-top refractive spatial beam shaping device, Newport GBS-AR14 is selected for spatial shaping. This passive device is identified to be the most suitable in terms of technical feasibility, simplicity, and reliability for use in high average power laser system. For longitudinal shaping, pulse stacking using birefringent crystals is chosen since it is relatively simple and provides stable pulse shaping. Although it has limited parametric flexibility, for well known input laser parameter, it is possible to achieve the required longitudinal profile with this technique.

A passively mode-locked Nd-vanadate laser oscillator (Time-Bandwidth Cheetah-X) is presently used for testing the refractive beam shaper module. The parameters of this laser resembles closely to the one planned to be used for the ERL experiments. It delivers-polarized laser pulses at 532 nm wavelength with average power of 2.5 Watts at a repetition rate of 81.25 MHz. The pulse duration was measured to be 10 ps FWHM by using an autocorrelator. The beam waist diameter was measured to be 1.3 mm with an ellipticity of ~0.97 and a beam divergence of ~0.15 mrad using a CCD camera (DataRay USB TaperCamD20-15). This camera has a tapered pixel array size of 15.8x15.8 mm, sufficient for the examination of uniquely large spatial beam shapes. A home-built repetitively scanning auto/cross-correlator is employed to measure the laser pulse width before and after the beam shapers.

TECHNICAL PROGRESS AND RESULTS:

In the first year of the project, the spatial profile of the laser beam was converted from a Gaussian to a flat top using passive refractive optics. Subsequent work focused on shaping the temporal profile, evaluating the optimal sequencing of components, establishing the tolerances and transporting the beam over long distance by relay imaging to maintain the modified shape.

Figure 1 Schematic of experimental arrangement



The experimental setup is shown in Fig. 1. The laser beam was first split into two using a 50% beam splitter, passed through two delay lines (arms) and then re-combined and focused on a type II second harmonic crystal (KDP) for auto and cross-correlation measurements. In one arm of the cross-correlator, a stack of three YVO4 birefringent crystals C1, C2, and C3 in decreasing crystal thickness of 24 mm, 12 mm and 6 mm respectively is positioned. By appropriately aligning the orientations of the crystals, a near flat-top pulse profile with

FWHM duration of ~ 53 ps was obtained. It has a rise and fall time of ~ 10 ps as dictated by the initial pulse width. The intensity modulation over the flat-top region is calculated to be $\sim 9\%$ (rms). Figure 2 depicts the experimental cross-correlations, the corresponding de-convoluted laser pulse shape, and the theoretically calculated pulse shape for a static phase of $\pi/2$ between all interfering pulses. The experimental cross-correlation agrees reasonably well with theoretical calculations. The temporal shaper and the spatial shaper were then stacked together, the output beam was transported over 9 m by Keplerian relay imaging. Figure 3 shows the beam profiles of input beam, output beam at 10 cm from the beam shaper and the output beam at 9 m from the beam shaper after relay imaging, along with expected profiles based on simulations using the computer code ZEMAX. At a distance of 10 cm away from the π -shaper and at 9 m distance with image relay system, the intensity modulations in the measured spatial beam profile is calculated to be $\sim 7\%$ (rms) and $\sim 10\%$ (rms) respectively over the plateau region. The optical transmission of the π -shaper is measured to be $\sim 92\%$. The tolerance on the angular misalignment (or tilt) and laser beam de-center (or beam lateral offset) relative to the axis of π -shaper are ~ 0.5 mrad and ~ 20 μ m respectively. Similarly, the tolerance on the input beam size is ~ 60 μ m at the optimum beam waist diameter of 4.7 mm.

Figure 2: Temporal profiles of the shaped pulse and input pulse

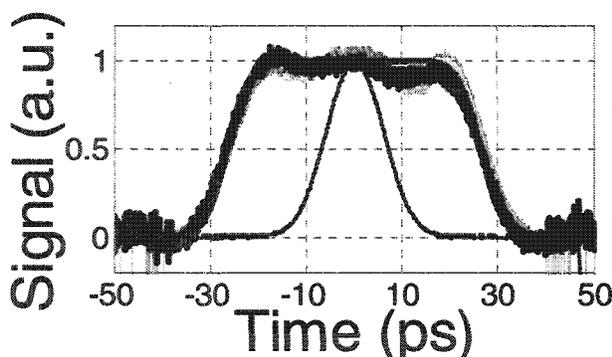
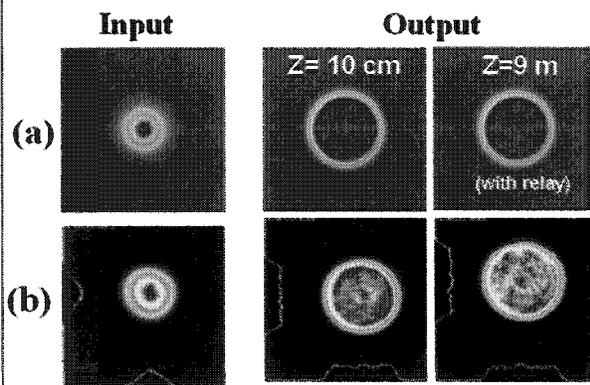


Figure 3 Input and output profiles after beam shaping



The future work will be directed towards shaping the ultraviolet (UV) beam of the ERL laser. The choice of the crystals and their dimensions are expected to change for the UV beam.

Furthermore, although the laser parameters of the ERL and the TBWP lasers are similar, they are not identical, requiring additional modifications to the beam shapers.

The techniques developed in this project will be useful in a number of applications. The laser beam shaping is an enabling technology that is needed for any high current low emittance electron beam source, especially RHIC II, eRHIC, ILC and future light sources.

Surface Engineered and Core-Shell Nanowires: Nanoscale Building Blocks for Third Generation Photovoltaics

LDRD Project 07-023

Peter Sutter, Eli Sutter, and Nicholas Camillone, III

PURPOSE:

Nanostructures, in which reduced spatial dimensionality and quantum confinement modify the intrinsic electronic and optoelectronic properties of a given material, have a significant but as yet unrealized potential for performance improvements in photovoltaic (PV) devices. Semiconductor nanowires (NWs) are an important example of a self-assembled nanoscale material with potentially large impact on future PV device technologies. This project focuses on exploring the synthesis, electronic, and optoelectronic properties of semiconductor NWs with controlled surface termination, and of NW-based core-shell structures. The results will help establish a fundamental scientific basis for evaluating possible NW-based third-generation PV devices.

APPROACH:

We use *in-situ* transmission electron microscopy (TEM) to study the formation of NW heterostructures, and to establish the phase behavior of nanoscale metal alloy drops used in their synthesis. We further combine the synthesis of novel NW-based architectures, such as surface-passivated and core-shell NWs, with electrical transport and photo-transport measurements on individual NWs. These measurements take advantage of the unique instrumentation available at the Center for Functional Nanomaterials (CFN), including nanofabrication facilities, electron microscopes, a UHV Nanoprobe, and a variable-temperature photocurrent microscope.

TECHNICAL PROGRESS AND RESULTS:

While the activities in NW synthesis and processing, initiated in the previous year, were continued successfully, we have now successfully performed measurements of single NW electrical and opto-electronic properties. Examples of key results obtained in the second year are given below.

Phase diagram of nanoscale metal alloy catalysts used for NW growth

TEM experiments at elevated temperatures on single NWs were used to determine the phase diagram of nm sized Au-Ge alloy drops, key for understanding and tailoring NW synthesis. Our observations show substantial deviations from the Au-Ge bulk phase diagram, in particular a strongly suppressed liquidus line and increased Ge solubility, for the nanoscale drops (fig. 1).

These results have important consequences on NW synthesis in general. For example, using the measured phase diagram we were able to demonstrate a process that changes the diameter of NWs during growth. This capability provides a novel approach to tailoring the electronic properties of NW devices.

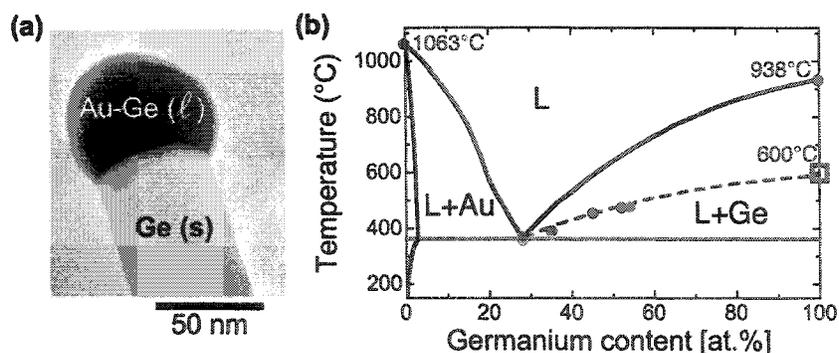


FIG. 1 – Determining the phase diagram of nm-sized Au-Ge drops.

(a) TEM image of a liquid Au-Ge alloy drop supported by a solid Ge NW.

(b) Comparison of Au-Ge bulk (solid lines) and nanodrop phase diagrams (dashed line).

Selective growth of Ge NWs by thermal evaporation

We have developed a novel synthesis method for Ge NWs, based on thermal evaporation of Ge-oxides at low source temperatures. The method not only provides high quality nanomaterials for transport and photo-transport measurements, but it constitutes a scalable process that could be used for mass-production of group IV semiconductor NWs for low-cost applications, such as photovoltaics. In the future, the method will be extended to include other NW materials (e.g., Si) and more complex materials and geometries, such as doped NWs and NW heterostructures.

Single NW electrical and photocurrent measurements

Single NW transport measurements in ultrahigh vacuum were developed to determine key materials and device properties of NWs and NW heterostructures. As a result, we are now able to routinely measure the resistivity and field-effect mobility of one-dimensional materials with diameters below 50 nm.

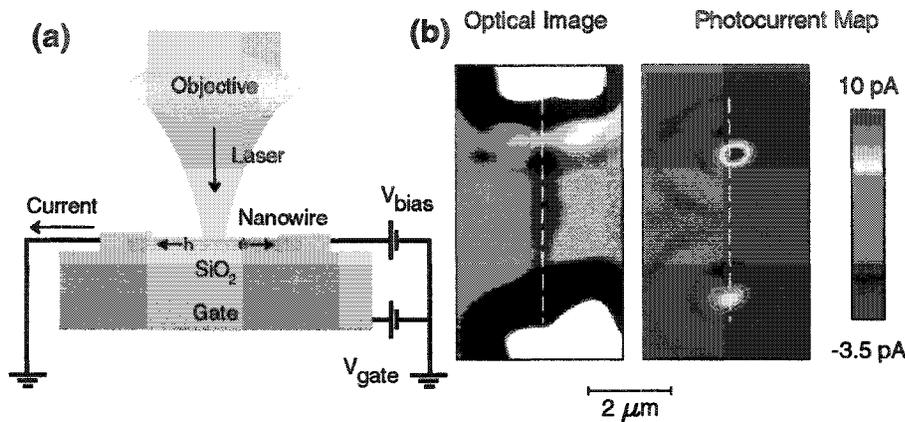


FIG. 1: Photocurrent mapping in a single Ge NW device. (a) Schematic of the photocurrent microscope. (b) Optical reflectivity image and photocurrent map measured at room temperature on a single Ge NW field-effect transistor.

Sensitivity to defect states at the surface is a factor that strongly affects NW device performance. The associated effects include, for instance, near surface band bending, which leads to a depletion of charge carriers and the separation of photo-generated electron-hole pairs. Electron-hole recombination mediated

by trap states, another surface effect, can cause strong reductions in carrier lifetimes and diffusion lengths. An important objective of this project is to understand and control such phenomena in semiconductor NWs.

To study the optoelectronic properties of single NWs, a cryogenic confocal optical microscope has been converted into a photocurrent microscope. The system allows measurements of temperature-dependent and spatially-resolved photocurrent in NW transistors, as shown in fig. 1. A tightly focused laser beam is scanned across a NW device, and the induced current is recorded as a function of position of the light source. The resulting map can be analyzed to determine electric fields inside the device, and to quantitatively extract charge carrier diffusion lengths.

To prepare device structures suitable for these measurements, electron-beam lithography, contact metallization, and annealing processes were developed; these activities leveraged the unique nanopatterning facilities at the CFN. Future work will concentrate on developing a quantitative understanding of the role of surface trap states in charge transport and photoelectric properties of NW devices, probed by temperature-dependent measurements on NWs with controlled surface modifications, such as oxidized or oxide-free NWs, as well as core/shell heterostructures.

Precision Assembly of Nano-Objects – Approaching Artificial Photosynthesis

LDRD Project 07-025

William Sherman

PURPOSE:

Recent studies have revealed that the efficient functioning of natural photosynthesis systems depends critically on the precise arrangement of molecular antennae and reaction centers on a biomolecular scaffold. The overarching goal of this project is to develop techniques that will allow nano-engineers to construct and manipulate opto-electronically active materials with a level of precision approaching that found in these natural systems. We have focused on the assembly of metallic and semiconductor NanoParticles (NPs) because of their well known tunable opto-electronic properties. We are using biomolecular scaffolds (primarily DNA) to direct formation, which have three key virtues: they assemble in parallel, they can form nanomechanical devices, and they form a wide variety of highly precise structures with feature sizes ranging from the 0.34 nm space between stacked base pairs up beyond the ~50 nm persistence length of a double helix. The natural continuation of this work is to create more precise and more complex structures, and to scaffold a broader variety of NPs and other guests such as fullerenes, and organic dyes. A more important follow-up will be the study and optimization of electron and energy transfer between scaffolded guests. Precision arrangements of NPs have been used to make low power computer processors, sub-wavelength yet efficient carriers of photonic signals, and SERS substrates, among a broad variety of other areas that could prove fruitful for future investigation.

APPROACH:

DNA nanostructures have typically been designed in such a manner that the underlying DNA double helices are minimally strained. Most structures with less than about 5% strain form well, but there were a number of low-strain structures that did not form as expected. We developed a method for analyzing assembly pathways that identified various traps that could prevent proper formation. Guided by this analysis method we built representatives of all three of the main categories of structures that had previously failed to form. All three were analyzed using Poly Acrylamide Gel Electrophoresis (PAGE) analysis, and arrays of structures were analyzed via Atomic Force Microscopy (AFM).

DNA nanostructures generally require about 10mM concentration of Mg^{2+} ions to help balance the negative charge of the DNA. Unfortunately, these ions tend to drive NPs to rapidly aggregate and thus fail to assemble on the scaffolds properly. Previous attempts to address these problems had generally only managed to stabilize the NPs in 1-3mM Mg, which strongly limits the ability to assemble scaffolded systems. Recent research had found that NPs coated with zwitterions resist aggregation in high concentrations of Na^+ ions. (A zwitterion is a molecular ion with both positively charged atoms and negatively charged atoms). We tried synthesizing gold NPs with a composite coating of zwitterions and DNA. The zwitterions were to minimize aggregation, and the DNA to allow the NPs to be connected to a DNA scaffold. The aggregation was observed via Dynamic Light Scattering (DLS). In collaboration with O. Gang.

NPs have previously been attached to DNA nanostructures in two ways: either via several strands of DNA per NP, or via a single strand of DNA per NP. With multiple strands, each NP could attach to a different number of binding sites, which lead to disordered structures. In contrast, with only a single DNA strand held each NP, then the NPs were free to move around over a range of

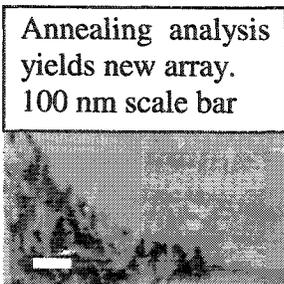
several nanometers. We devised an array based on tight clusters of triplets of binding points separated by large spacings. This way each NP is firmly held in place by exactly three anchors in each cluster on the scaffold. Assembly of the scaffold components was observed by PAGE, and then the scaffold and the scaffold/NP assemblies were deposited on mica or carbon grids and observed by AFM and Scanning Transmission Electron Microscopy (STEM). This work with O. Gang.

Two strands of DNA can hybridize together to form a double helix even if they are not perfect matches for one another. The two strands can be separated, however, if a third strand is added to the solution that is a superior match for one of the first two. This 'fuel strand' technique allows specific removal of strands and the subsequent reconfiguration of DNA complexes and any scaffolded guests. We built a DNA linear actuator and inserted it between gold NPs. As the actuator was expanded and contracted, the size of the clusters was observed via DLS, and the average surface to surface separation between NPs was observed via Small Angle X-ray Scattering (SAXS). This work was done closely with O. Gang, D. Nykypanchuk and M. Maye.

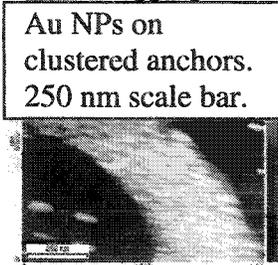
A number of smaller side projects have been supported by this LDRD, including work published on scaffolding quantum dots on toroidal protein structures with H. Xie, Y.-F. Li, H. Kagawa, J. Trent, M. Cotlet, and B. Swanson; a collaboration with P. Freimuth on DNA/protein hybrid scaffolds, and a project to develop fine control of angles in DNA nanostructures.

TECHNICAL PROGRESS AND RESULTS:

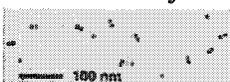
A few months of work were done before fiscal year 2008, so no projects had been completed.



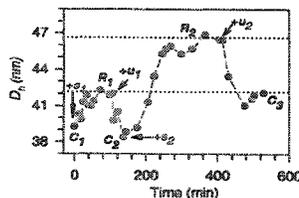
The annealing analysis successfully allowed the construction of numerous structures previously thought unstable, such as the striped array shown in the AFM image at left. DLS observations showed that the zwitterion/DNA coatings on Au NPs completely prevented aggregation for at least 15 hours in standard 10mM Mg solution, as compared with about 10 minutes for the commonly used surface coating. Au NPs were successfully attached to a DNA array with clusters of three anchor points per NP. At right is an AFM image of such a structure. The NPs are too close together for easy analysis via AFM, so we have recently switched to scanning electron microscopy and have been getting much clearer images of large, well ordered arrays of NPs. The NPs separated by DNA actuators formed nice dimers as shown in the transmission electron micrograph at left. DLS revealed the dimers expanded over a range of about 9 nm between contracted state C2 and extended state R2 (lower graph). This is close to the expected range of motion of 7nm, and is comparable to our data on larger clusters of NPs, though the large clusters reacted with lower speed and yield.



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The highlights of the past year are the successful annealing analysis, which solidifies the theoretical underpinning of the entire field of DNA nanostructures; and the creation of the zwitterion/DNA coating for NPs, which will bring the full

power of DNA scaffolding to a broad assortment of NPs. The mounting of NPs on DNA clusters will allow for angular manipulation of NPs, which will open up new avenues of research, particularly in the angular dependence of energy and electron transfer rates.

Photocatalytic Carbon Dioxide Reduction to Methanol using Metal Complexes with an NADH Model Ligand

LDRD Project 07-027

Etsuko Fujita and James T. Muckerman

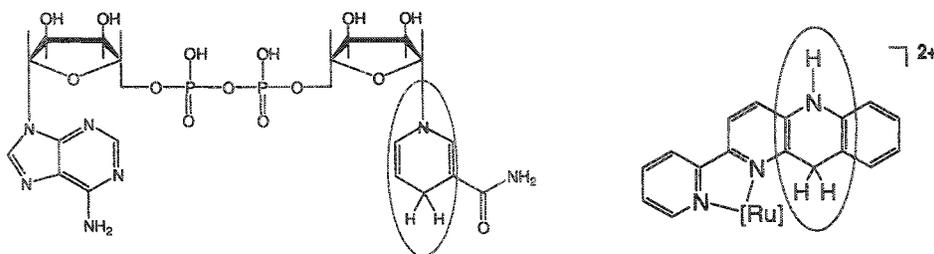
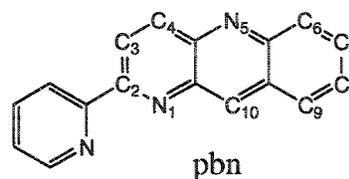
PURPOSE:

The aim of this project is to explore CO₂ reduction to methanol employing a new methodology to photochemically produce hydride donors using functionalized metal complexes with a reduced nicotinamide adenine dinucleotide (NADH) model ligand. This new bioinspired approach seeks artificial photosynthetic systems for catalytic hydrogenation/reduction of CO₂ beyond CO and HCOO⁻ (which have been produced as the only products of photoreduction of CO₂ in homogeneous systems). This is high-risk research, but it is a very important area to investigate to secure future energy needs. This research, if successful, would not only produce a valuable chemical fuel from solar energy, it would recycle the carbon dioxide released when it is burned.

APPROACH:

Stoichiometric chemical conversion of a coordinated CO to methanol or methane using NaBH₄ has been reported for [Ru-CO]²⁺ → [Ru-CHO]⁺ → [Ru-CH₂OH]⁺ (Ru = Ru(bpy)₂(CO)) and for [Re-CO]⁺ → Re-CHO → Re-CH₂OH → Re-CH₃ (Re = Re(Cp)(NO)(CO)). This raises the question: Can we replace NaBH₄ by a renewable (*i.e.*, visible-light-generated) hydride donor to produce solar fuels?

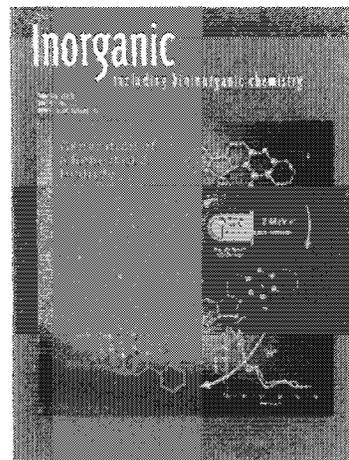
A combination of experimental and theoretical approaches is being pursued to investigate the mechanism and kinetics of several promising transition-metal complexes with NADPH-model ligands for the photocatalytic reduction of CO₂ to methanol. In particular, rhenium and ruthenium complexes containing the pbn (*i.e.*, 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) ligand may offer promise as photocatalysts for the hydride-transfer reactions required to reduce CO₂ beyond CO, all the way to methanol. This approach will create new directions for the solar energy conversion of CO₂ into energy-rich fuels through *low energy pathways* using functionalized transition-metal complexes as hydride ion donors. The basic knowledge obtained through this study – *e.g.*, the energetics of coupled proton and electron transfer for redox leveling and proton addition and removal, and catalysis *via* hydride transfer, and bond forming/cleavage – will be essential for designing more effective proton-coupled multi-electron-transfer reactions for fuel production.



Structures of NADPH and a ruthenium complex with an NADPH-model ligand (pbnHH)

TECHNICAL PROGRESS AND RESULTS:

We have demonstrated that a hydride donor $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ is cleanly formed by the reductive quenching of the metal-to-ligand charge-transfer (MLCT) excited state of $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ by triethylamine upon irradiation with visible light ($< 600 \text{ nm}$) with a quantum yield of 0.21 at $\lambda = 355 \pm 6 \text{ nm}$. These results open new opportunities for the photochemical generation of strong hydride donors for the *catalytic* hydrogenation of organic molecules (and hopefully CO_2 and related species) by visible-light irradiation as Nature does. This finding has also prompted us to carry out more detailed studies on the mechanism of the photochemical formation of the $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ species. The resulting publication of a comprehensive mechanistic study of $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ conversion into $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ using steady-state and transient radiolytic and photochemical techniques was featured as a cover article of *Inorganic Chemistry* (May 19 issue, 2008).



While $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ can transfer the hydride to Ph_3C^+ , the bulky environment around the hydride site on $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ may impose kinetic limitations for the hydride transfer ($k = 4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$). $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ can not transfer a C-H hydride to M-CO or CO_2 . However, our theoretical investigation predicted that its one-electron-reduced radical species $[\text{Ru}(\text{bpy})_2(\text{pbnHH}^{\bullet-})]^+$ is a better hydride donor and can transfer a hydride to M-CO. We found that $[\text{Ru}(\text{bpy})_2(\text{pbnHH}^{\bullet-})]^+$ can be produced photochemically by reductive quenching of the excited state species and is reasonably stable in acetonitrile solution. We will test to see if M-CO can be photochemically converted to M-CHO⁻ using this highly reduced species that pools the energy of 3 photons.

We have also prepared several new complexes including $[\text{Ru}(\text{pbn})(\text{tpy})\text{Cl}]^+$, $\text{Re}(\text{pbn})(\text{CO})_3\text{Cl}$ and $[\text{Re}(\text{pbn})(\text{CO})_3(\text{PCy}_3)]^+$, and have started examining the acid-base and electrochemical properties of the ground and excited states of these species.

Structure of Mass-Size Selected Nanoparticles by Scanning Transmission Electron Microscopy

LDRD Project 07-030

Michael G. White and Joseph Wall

PURPOSE:

The purpose of this project is to explore the atomic structure of small, supported nanoclusters utilizing high-resolution electron microscopy and scanning probe techniques (AFM, STM). This project addresses the critical need to understand how the atomic structure evolves from small clusters containing tens of atoms to larger particles whose structure mimics the bulk material. Our approach involves the coupling of novel methods for preparing nanoparticles over a very large size range (10 Å to 10 nm) with single particle imaging techniques (STEM, AFM, STM). The specific technical challenges involve (1) the development of a high-speed, 2D detector and software that enables high throughput, single particle diffraction at the Biology STEM; (2) the development of a vacuum load-lock system that allows transfer of air-sensitive samples between the deposition instrument in Chemistry and the scanning probe instrumentation at the CFN. If successful, this program would demonstrate the capability of probing the atomic structure of non-crystalline nanomaterials that could have significant impact on current nanoscience programs at BNL and future instrumentation developments at the CFN.

APPROACH:

We have recently developed new techniques for depositing metal and metal compound (oxide, sulfide) nanoclusters onto solid supports that act as model nanocatalysts that are key to our DOE funded research in energy-related catalysis. Methods include the use of a novel, size-selected cluster deposition instrument that can pre-select mass (size) and chemical composition of nanoclusters prior to deposition [1] and the use of block co-polymer templating which is a benchtop technique that provides independent control of nanoparticle size *and* interparticle spacing (density) [2]. The former is useful for small clusters up to a few hundred atoms (1-2 nm), while the latter technique can provide larger nanoparticle sizes in the range of 1-20 nm. Both techniques yield bare (unprotected) nanoparticles supported on metal oxide substrates (e.g., alumina, titania, silica), typical of heterogeneous catalysts. Our ability to understand and model the reactivity of such nanoparticles, however, is severely hampered by the lack of direct structural information, either in the gas-phase or deposited on surfaces. The two main obstacles are (1) the difficulty of imaging the atomic structure of small non-crystalline or 3D nanoparticles, and (2) practical limitations that require the sample to be exposed to air in order to load it into high resolution imaging instrumentation (STM, AFM, TEM). Air exposure can result in oxidation of the catalyst nanocluster and/or contamination of the nanoparticle and substrate with background contaminants (airborne organics) that often can't be removed without also altering the nanocatalyst surface.

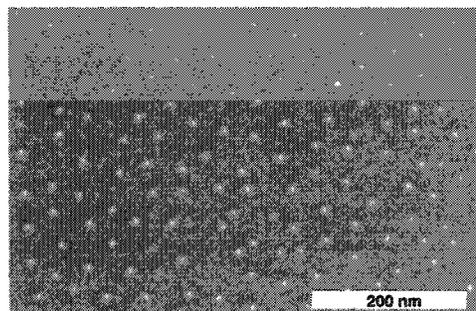
In this LDRD project, we intend to combine our newly developed nanoparticle synthesis techniques with the imaging capabilities of the scanning electron microscope facility in Biology (STEM; in collaboration with Joe Wall) and state-of-the art scanning probe instruments (STM, AFM) at the CFN (in collaboration with David Starr and Peter Sutter). Wall's group has extensive experience with imaging small metallic clusters and the use of convergent beam electron beam diffraction (CBED) for direct structural characterization of individual nanoparticles. In addition, we will develop and install a vacuum suitcase sample transfer system onto the cluster deposition apparatus in Chemistry so that samples can be moved to the CFN

facility without exposure to air. The latter is based on a high speed getter pump (400 l/sec for N₂) and will use sample holders that are compatible with the RHK-STM at the CFN. The samples will be loaded directly into the STM for atomic imaging and investigations of thermally-induced diffusion and sintering.

TECHNICAL PROGRESS AND RESULTS:

2008-2009

Over the last year we focused on the development of the block-copolymer method for the preparation of metallic nanoparticles for STEM imaging experiments. This approach uses a hydrophobic polymer block (polystyrene) that is covalently linked to a hydrophilic polymer block (polyvinylpyridine) that forms micelles in a non-polar solvent. These “reverse” micelles act as nanopores for metal cluster growth. Subsequent reduction of the metal cations and removal of the polymer matrix results in nanoparticles whose size and spacing can be independently controlled by varying the relative molecular weights of the two polymer blocks. We have successfully demonstrated this approach for the preparation of various sized nanoparticles of Au, Pd, and Rh on SiO₂ surfaces and various TEM grids (holey carbon, SiO₂/W). Over the next few months, we intend begin our first imaging and CBED experiments using the Biology STEM. It is expected that these first diffraction experiments will make use of new multi-element silicon area detector and integrated readout electronics recently developed by BNL Instrumentation.



SEM image of Au nanoparticles supported on a silica substrate prepared by the block copolymer approach. The average particle size is 12.4nm ± 6.4nm.

We have also recently purchased a UHV capable “vacuum suitcase” (Tectra, Germany) for sample transfer from our size-selected cluster apparatus in chemistry and the STM instrumentation at the CFN. After installation and testing on our cluster apparatus in chemistry, we will try our first sample transfers to the CFN where they will be loaded and imaged on the RHK STM instrument. Our initial goal is to study supported nanoclusters of molybdenum sulfide that act as models catalysts for hydrodesulfurization. The STM imaging experiments will be used explore cluster dispersion, cluster structure and thermally-induced morphology changes. Such information will provide crucial information on the cluster substrate interactions as well the fate of the clusters under reaction conditions (high temperature).

References:

1. J. M. Lightstone, M. J. Patterson, P. Liu, J. C. Lofaro and M. G. White, *J. Phys. Chem. C*, 112, 11495 (2008).
2. J. P. Spatz, S. Mossmer, C. Hartmann, M. Moller, T. Herzog, M. Krieger, H. Boyen, *Langmuir* 16, 407 (2000).

Synthesis of Conjugated Polymers for Fundamental Questions in Solar Energy

LDRD Project 07-032

John Miller and Xiao-Qing Yang

PURPOSE:

This project intends to create conjugated molecular materials, “molecular wires” and to test whether charges and excitons can migrate efficiently over long distances within such “wires.” It is specifically focused on transport within single, long chains as distinguished from transport that requires hopping from one chain to another. If efficient, such transport could be utilized to design new, highly efficient solar cells.

APPROACH:

Two principal barriers to high efficiencies in organic photovoltaic cells are 1) Insufficient charge mobilities and 2) Short, 10 ns or less, exciton diffusion lengths. Many discussions in the literature describe the short exciton diffusion length as a fact- one almost gets the feeling it is almost a law of nature. On the other hand no fundamental principle requires such a limit on exciton diffusion. This LDRD is based on the proposal that both charges and excitons can transfer over very long distances in conjugated polymer “molecular wires,” beginning with tests in solution which are simplest to implement. The approach would utilize conjugated polymers having appended “trap” groups intended to capture charges or excitons.

Polythiophenes are one of the most widely used materials at present for organic photovoltaic cells. Short-term targets were synthesis of polythiophenes having appended groups that could capture either electrons or excitons in the polymers: We hoped to create dual-purpose molecules in which different experiments could probe both questions. The appended groups (traps) would be distributed randomly along the polymer chains with one such trap group for each ~20 repeat units. That number would then be adjusted.

A second goal was to create such molecules with enhanced solubility in non-polar media to facilitate experiments there.

Following synthesis, we aimed to perform two initial types of experiments, both in fluid solution:

- a) Electrons would be attached to polymer molecules at the LEAF accelerator while monitoring formation of polymer anions and their disappearance by transient absorption,
- b) Photoexcitation of the polymers would be performed and transport of excitons to the traps and their capture there would be measured by quenching of fluorescence.

The first targets were synthesis of polythiophenes having radicals attached. These radicals were intended to function as either electron or exciton traps.

TECHNICAL PROGRESS AND RESULTS:

Results in the First Year

1. Synthesis of monomer groups having long or branched alkyl chains to enhance solubility and monomer groups having traps attached. This was followed by synthesis of polythiophenes using these feedstocks with unprecedented solubility in nonpolar solvents.
2. Polymerization of monomers into polymers with TEMPO radicals intended to serve as traps. No capture of electrons or excitons was observed.

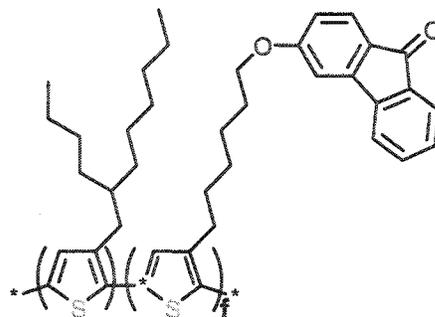
- Thiophene monomers were created with appended dinitrobenzene trap groups. Experiments with these monomers showed that the dinitrobenzene groups captured electrons to produce radical anions of dinitrobenzene. Polymers created from these monomers did not show trapping of charge or excited states.

New Results in the Second Year

- Varied thiophene monomers and polymers were created with appended dinitrobenzene trap groups. Unfortunately no capture of electrons was observed. It is our suspicion that somehow the dinitrobenzene groups interfere with incorporation of the thiophene monomers into the polymer.
- Experiments at LEAF showed that the branched side chains which yielded polymers of excellent solubility in non-polar liquids like isooctane did lead to very fast electron capture. This exciting result makes possible experiments with very fast time resolution if suitable trap groups can be introduced.
- New monomers were created having fluorenone trap groups attached to thiophenes. Polymerization of these also did not lead to electron capture, although the monomer did capture electrons. Several other polymerizations were attempted, but many failed. These are listed in a table below.

number	Monomer	Polynmerizations
1	19-90 3-hexadecylthiophene	That did not succeed
2	19-88 3-(3,7-dimethyloctyl)thiophene	
3	19-93 3-(2-butyloctyl)thiophene	3 + 4
4	19-72 4-hydroxy-TEMPO 3-thienylacetate	2 + 4
5	19-133 2,5-dinitrophenyl-3-thienylacetate	3 + 5
6	20-24 3-(6-pyranylohexyl)thiophene	2 + 5
7	20-28 benzyl-3-thienylacetate	2 + 3-thienyl ethanol
8	20-35 3-(2-benzyloxyethyl)thiophene	2 + 6
9	20-36 3-(6-benzyloxyhexyl)thiophene	2 + 7
10	20-77 3-(2-(2,4-dinitrophenoxyethyl)thiophene	2 + 9
11	20-92 2-(6(3-thienyl)hexyloxy)-9-fluorenone	2 + 11
12	20-39 3-(6-(3-bromohexyl)thiophene	

- Monomers were with bromo substituenets were polymerized. These were then reacted with groups containing fluorenone traps, to attach fluorenone moieties AFTER polymerization. The polymers thus created utilized the butyloctyl side chains that confer excellent solubility. Polymerizations were carried out with the fraction, $f=0.5, 0.2$ and 0.1 , of bromo monomer, which is a precursor to which the fluorenone is attached. At this writing, the fluorenones capture electrons and produce fluorenone radical anions. But the amount of electron capture does not correlate in a sensible way with the fraction f , of fluorenone containing monomer. The results are encouraging, but more work is needed to: a) Determine how many fluorenones are actually attached, b) Optimize the conditions to make the synthesis more predictable, and c) determine the presently unknown average lengths of the polymers, including whether they change in the step that adds the fluorenone.



Ultra-thin Graphite Analog Compounds

LDRD Project 07-035
Tonica Valla

PURPOSE:

The purpose of this LDRD is to develop methods of synthesis of ultra-thin graphene layers, to probe their transport and spectral properties and to explore possibilities of modifying those properties with the ultimate goal to “magnetize” graphene and to explore possibilities of making spin-polarized transport devices that could be used in spintronics applications.

APPROACH:

We have developed several different methods of synthesis of graphene layers:

1. high temperature annealing of SiC(0001) in an ultra-high vacuum
2. mechanical exfoliation of HOPG on SiO₂/Si
3. pyrolysis of ethylene/methane on Ir(111) surface

Electronic structure and other spectral properties of these systems have been measured. Transport properties of the first two systems have also been measured. Effects of magnetic and electric fields as well as modifications of electronic properties due to different adsorbates/substrates have been studied and ways of modifying graphene’s properties are being explored in order to find the optimal system for applications in devices.

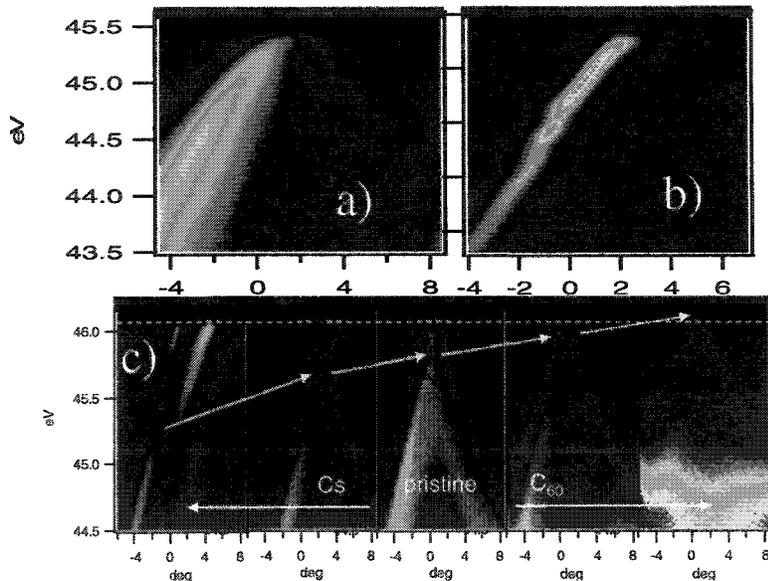


Fig. 1 ARPES near K point from a) an exfoliated graphene bilayer on SiO₂/Si, b) graphene monolayer on Ir(111) and c) a graphene bilayer on SiC. In c) a pristine sample (middle panel) was doped with Cs (left) and C₆₀ (right). A shift of Dirac point is indicated by yellow arrows.

adsorbates induce charge transfer into the graphene layers, cause weak or strong localization and open the gaps in the electronic structure. All of these effects allow modification of graphene properties in a targeted manner. For example, by adsorbing C₆₀ molecules onto a graphene bilayer, holes are introduced into its bands and a gap can be open and tuned to the chemical

TECHNICAL PROGRESS AND RESULTS:

After a successful synthesis of graphene layers on different substrates, we have focused on studying their physical properties and on fabrication of devices used in transport experiment. ARPES is the most direct probe of the electronic structure and we have used it on all three synthesized systems to check the quality and the doping level of our graphene layers and to study the interaction of the graphene layers with various adsorbates.

We have demonstrated that our graphene layers are of extremely high quality and that

potential. Therefore, a graphene bilayer (a metal) can be turned into an “insulator” by adsorption of C_{60} molecules. Similarly, by adsorbing a ferromagnetic species, a graphene layer might become magnetized, i.e. graphene’s electronic states could become spin-split. The experiments in which ferromagnetic adsorbates and/or substrates will be used to induce spin splitting of graphene states are planned for the very near future. In the meantime, we have done

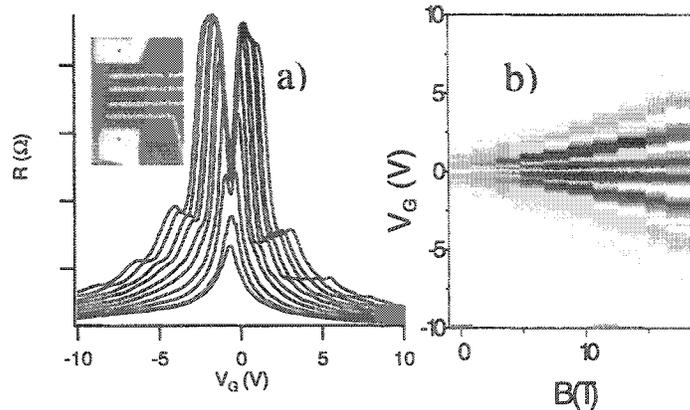


Fig. 2. a) Resistance of a graphene flake (shown in the inset) as a function of gate voltage, measured in parallel magnetic field varied from 0 T (bottom curve) to 18 T (top curve). b) dR/dV_g shown on a false color scale as a function of gate voltage and magnetic field. Dispersing states are Landau levels whose splitting increases with B .

transport measurements in magnetic field at National Magnet Lab (jointly with a TechMat Project) as the similar spin splitting could be induced by a strong parallel magnetic field. These experiments have been performed on devices fabricated by L. Zhang and J. Camacho at the CFN, showing a state of the art capabilities of our facilities and the World class quality of our devices. Mobilities of our graphene layers were amongst the highest ever measured on SiO_2 substrate. The results (Fig. 2) show a rich behavior with many dispersing states, still not completely understood by current theories. However, a small Zeeman splitting near the Dirac point indicates that a much larger splitting could be induced by proximity to a ferromagnetic substrate/adsorbate.

In the remaining period of this LDRD we intend to:

- Reproduce the spin injection from ferromagnetic leads (Co, permalloy, etc) into the graphene layers.
- Induce the spin polarization in the graphene bands by “magnetic proximity” – by overlapping the graphene states with spin-polarized states in ferromagnetic substrates (EuO, Ferrimagnetic garnets, NiO, etc) and/or adsorbates (NiO, Fe, Co, etc).
- Measure transport and spectral properties of magnetized graphene layers.

We have become regular users of the CFN where our contact patterning and some transport, structural and spectral studies (nano-lithography, STM, AFM, Raman) are regularly being done. Our ARPES studies have been done at the NSLS and several other synchrotrons (ALS, Elettra). We have established strong collaborations with several CFN groups, Condensed Matter Theory group and Surface Science group from Institute of Physics, Zagreb.

Lipid-Coated Nanoparticles and Their Interactions with Lipid Membrane Surfaces

LDRD Project 07-036

M. Fukuto, L. Yang, and O. Gang

PURPOSE:

Exploring methods to render inorganic nanoparticles (NPs) both bio-compatible and bio-functional is important for facilitating biomedical and biomimetic-device applications of NPs. One method that is likely to be highly effective and versatile is to coat NPs with lipid bilayer or monolayer membranes. Lipid membranes provide a natural environment for membrane proteins and also have the potential to endow NPs with the ability to adhere to and penetrate into the cells by means of membrane fusion. This project aims to (I) explore methods for coating NPs of various sizes with simple lipid mono- or bilayer membranes, and (II) investigate the interactions of lipid-coated NPs with simple model lipid membrane surfaces.

APPROACH:

There already exist well-developed techniques for depositing lipid layers on *planar* solid substrate-aqueous solution interfaces (e.g., vesicle fusion method). We apply these to the highly curved surfaces of NPs and examine the effect of surface curvature on the ease and uniformity of lipid-layer coatings. NPs to be used are gold NPs (diameter > 5 nm dia.) and commercially available silica spheres (dia. > 20 nm). Mat Maye, synthesized gold NPs. Sumit Kewalramani, the LDRD-supported postdoctoral associate in CMPMSD, carries out the lipid-coating and dynamic light scattering experiments to extract size distributions and test the formation of lipid membrane around NPs.

Part II of our study will elucidate the interactions between the lipid-coated NPs (LCNPs) and other lipid membrane surfaces, which include a single lipid bilayer or monolayer at planar substrate-buffer or buffer-vapor interfaces. Lipid mixtures will be used to explore and tune the interactions that are based on, e.g., protein-mediated binding and electrostatic forces. Establishing expertise with these membrane surfaces is also an important aspect of this project. Flat membranes are well suited for initial studies because of their simple geometry and because we have the infrastructure for appropriate in-situ characterization tools (optical microscopy, AFM, synchrotron x-rays).

TECHNICAL PROGRESS AND RESULTS:

Following the arrival of S. Kewalramani in October, 2007, we initiated our efforts to coat NPs with lipid membranes [the goal (I) above]. The coating with lipids was tested for hydrophobic alkane-capped gold NPs (diameter 6 nm) and for hydrophilic silica NPs (dia. 30 and 80 nm). For hydrophobic gold NPs, either (a) an organic (toluene) solution of NPs or (b) a solution-cast film of NPs was either (i) mixed directly with an aqueous lipid vesicle solution, via ultrasonication followed by stirring, or (ii) mixed in steps, first with organic lipid monomer solution and then with aqueous buffer. Although these different mixing procedures were attempted, none of them resulted in coating of 6 nm hydrophobic gold NPs with lipids. For hydrophilic silica NPs, their suspension in water was mixed directly with an aqueous lipid vesicle solution. The light scattering data (Fig. 1) suggests the formation of a lipid layer around 80 nm silica NPs. It may be that larger and more hydrophilic NPs are more easily coated by lipid membranes. Experiments on hydrophilic, citric-acid-protected gold NPs with relatively large mean diameters (41 and 74 nm) are currently in progress.

For the goal (II) above, our efforts in FY07 were focused on gaining experience with lipid membranes that consisted of binary mixtures of a neutral lipid and another lipid possessing a special property, such as a charged head group or a protein-binding ligand. In particular, we examined the role of surface ligand (biotin) density within a lipid monolayer in controlling the 2D assembly of a model protein, streptavidin, at the aqueous buffer-vapor interface. The protein has two ligand-binding sites on one side and two more sites on the opposite side. The most significant result in FY07, based on Brewster-angle microscopy (BAM) and grazing-incidence x-ray diffraction (GID), was the observation of a threshold surface ligand density for 2D protein crystallization. However, its origin as well as the state of bound proteins below the threshold ligand density remained uncertain due to the lack of information about the amount of proteins adsorbed at given ligand density. In FY08, we carried out x-ray reflectivity (XR) measurements and extracted the dependence of protein adsorption on the surface ligand density (Fig. 2). The results indicate that the *cooperative* binding between a streptavidin and two biotin-bearing lipids is the primary mechanism for the adsorption. That is, the adsorbed streptavidin is almost always doubly bound, and both singly bound and nonspecifically adsorbed proteins are nearly absent even at low ligand densities where crystallization does not occur. Taken together, the XR/GID/BAM results imply that the interface-bound proteins share a common, fixed orientation relative to the surface normal and that the 2D crystallization occurs when the lateral *protein* density reaches 50-70% of the value in the 2D crystal (Fig. 2). This study is significant in that it quantitatively demonstrates the importance of both well-defined molecular orientation and high lateral packing density to the 2D crystallization of proteins. Moreover, it shows how the property of lipid membrane can be tuned to control the 2D assembly of nano-scale objects.

The milestones that we aim to achieve in FY09 are: (1) to continue to extend the capability for producing LCNPs; and (2) to study 2D assembly of these LCNPs on a lipid membrane at substrate-buffer or buffer-vapor interfaces. Our experience with the lipid-assisted 2D protein assembly (above) should greatly aid us in our efforts toward the milestone (2).

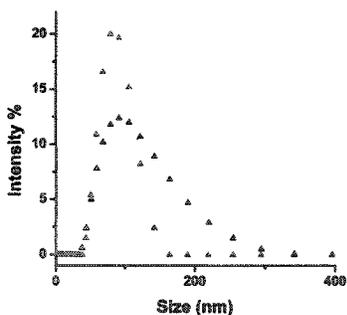


Fig. 1. Size distributions, based on light scattering, for 80 nm silica NPs in HEPES buffer at pH 8 before (blue symbols, peak at 85 nm) and after mixing with DOPC lipid vesicles (brown symbols, peak at 91 nm). The peak shift by ~6 nm is roughly of the same order of magnitude as the thickness of a lipid bilayer. For NPs with lipids (brown), the tail on the right side may be due to the presence of multiple lipid-bilayer coatings for some NPs or to some degree of aggregation of NPs.

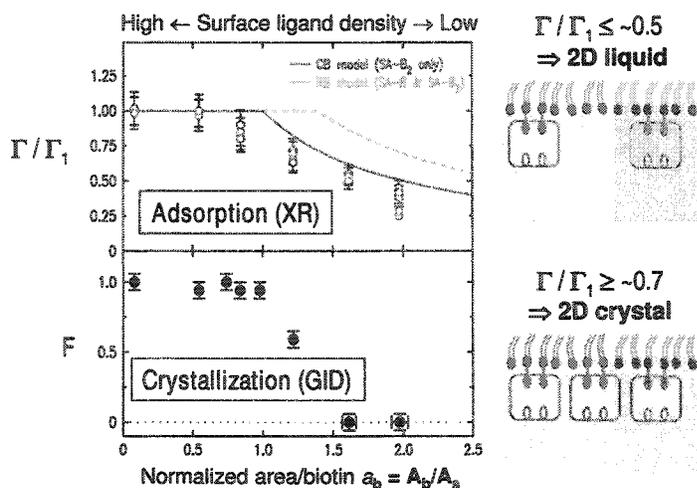


Fig. 2. Effects of surface ligand density on adsorption (left top) and 2D crystallization (left bottom) of the protein streptavidin bound to a ligand-bearing lipid monolayer on buffer solution, where Γ/Γ_1 = relative adsorption; F = fraction of illuminated spots showing GID peaks for 2D crystal; A_b = area per ligand (biotin) in lipid layer; and A_s = area per upward binding site in 2D protein crystal. Theoretical curves (left top) represent the cooperative binding model allowing only doubly bound proteins (red/solid line) and the random binding model allowing both doubly and singly bound proteins (green/dashed line).

Angle-Resolved Time-of-Flight Ion Scattering Spectroscopy from MBE-Grown Oxide Thin Film Surfaces

LDRD Project 07-038

Adrian Gozar

PURPOSE:

We use the time of flight (TOF) low energy ion scattering and recoil spectroscopy (ISARS) technique in order to get information about surface properties of oxide films grown by molecular beam epitaxy (MBE). In particular, these properties are primarily related to the composition and the structure of the topmost atomic layers. Such information can provide real-time feedback for epitaxy and information about the atomic layer-by-layer (ALL) growth of single phase films or heterostructures. So far we have used the TOF-ISARS technique for the study of films of high temperature superconductors (HTS), a class of strongly correlated electronic materials.

APPROACH:

The ALL-MBE system was used to synthesize HTS films, multilayers, and superlattices. The TOF-ISARS setup consists of a pulsed source generating K^+ ions with energies in the 7-13 keV range. The intensities are measured in the scattering plane by micro-channel plate and mass spectroscopy of recoiled ions (MSRI) detectors mounted at several fixed angles. The system allows for a continuous change in the azimuthal angle. Surface composition and termination can be studied by monitoring the change in the cross section as a function of angular scattering geometry and as a function of the layer-by-layer deposition sequence. Experimental data is compared to the semi-quantitative information obtained from classical trajectory simulations based on the binary collision approximation.

TECHNICAL PROGRESS AND RESULTS:

- TOF-ISARS oscillations: we checked if TOF-ISARS can be used to study the layer-by-layer growth by recording of what we named 'TOF-ISARS oscillations'. The most important real-time feedback during growth comes from reflection high energy electron diffraction (RHEED) and from monitoring the sequence and structure of RHEED oscillations which are observed during growth of atomically smooth films. However, electron diffraction is not chemically sensitive. TOF-ISARS data are shown in Fig. 1. They indicate that such oscillations can be used for studying deposition and real-time calibration of absolute rates for specific elements.
- Chemical profile at interfaces: we used TOF-ISARS to determine the chemical profile (cation interdiffusion) at interfaces in bilayer films where transport data indicates the existence of high temperature interfacial superconductivity. We studied the evolution of the Sr peak intensity during the growth of $La_{2-x}Sr_xCuO_4 - La_2CuO_4$ bilayer systems and we found that our data can put a limit of one unit cell for cation mixing, see Fig. 2. This is an upper bound because of subsurface scattering (that can be clearly seen also in Fig. 1 where the oscillations minima are not zero). A simple phenomenological model including such effects and assuming an interdiffusion proportional to the nominal difference in Sr concentration between adjacently deposited layers reveals indeed a more abrupt profile, consistent with transmission electron spectroscopy and soft X-ray diffraction data in superlattices. This is a great advantage because it can be done in-situ and does not involve either sample preparation or expensive instrumentation (e.g. synchrotron light) in order to obtain such important information. Substrate surface termination studies using

TOF-ISARS are planned for precise determination of the initial layer sequence and achieving defect-free interfacial layers in ultra-thin bilayer films (2-3 unit cells).

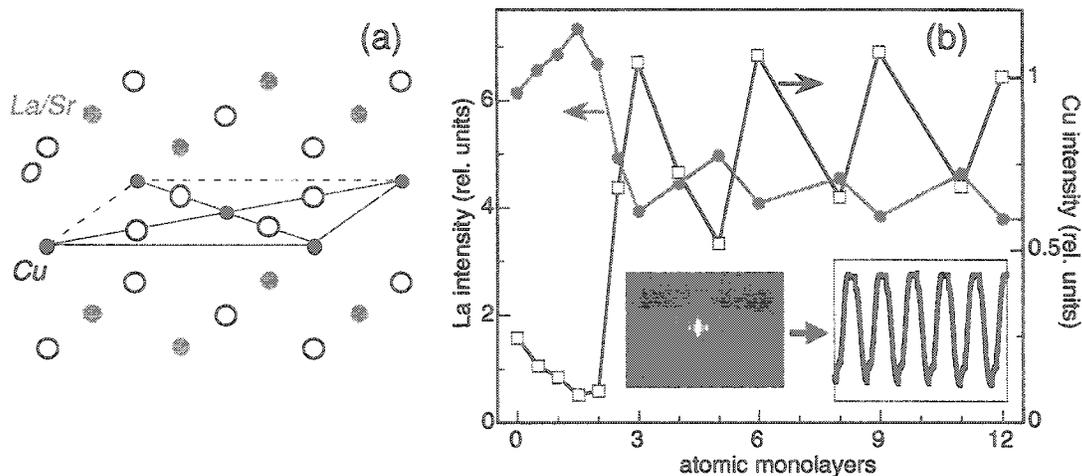


Fig.1: (a) The '214' structure of La_2CuO_4 (LCO) crystal. (b) TOF-ISARS oscillations: MSRI intensities of La and Cu peaks during the layer-by-layer deposition. Three atomic monolayers correspond to the structure in (a); the deposition sequence was $[2\text{LaO}-\text{CuO}_2]_{12}$ which corresponds to 6 unit cells of LCO. The inset shows typical RHEED oscillation pattern during growth of LCO films.

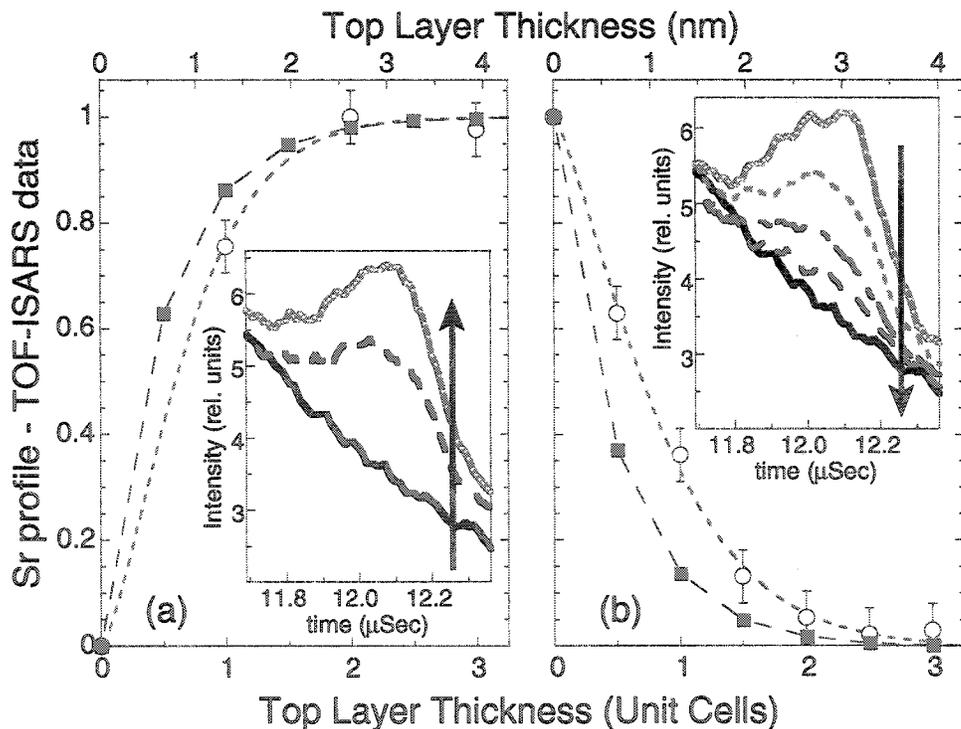


Fig.2: (a) TOF-ISARS data as a function of top layer thickness in a La_2CuO_4 (*I*) - $\text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4$ (*M*) (*I-M* bilayer film (the last letter denotes the top layer)). The main panel displays the normalized integrated intensity of the Sr recoil peak in *M* (open circles). The Sr concentration profile, estimated from a phenomenological model assuming sub-surface scattering, is displayed by filled squares. Dashed lines are guides for the eye. The inset shows the evolution of the Sr recoil peak with each unit cell of *M* deposited on the *I* bottom layer as recorded in the TOF data. (b) Same as (a), but on the *I* side of *M-I* structure.

Characterization of Enzymatic *O*-Acylation to Facilitate Biomass and Bioenergy Production

LDRD Project 07-047

Chang-Jun Liu

PURPOSE:

Enzymatic *O*-acylation is a common modification for plant cell-wall lignocelluloses. Acylation of lignocellulosic components changes cell wall structure, degradability, and ultimately affects the growth, development, and reproduction of plant feedstocks. The *O*-acylation and deacylation reactions also occur in the biosynthesis of a variety of wood-forming required secondary metabolites in trees. The addition of acyl groups on the non-structural secondary metabolites alters chemical stability and solubility, and influences their subsequent sequestration and storage. Despite the wide occurrence of *O*-acylation in plant metabolism and cell wall modification, the enzymes involved in this process remain largely elusive, and the precise biological roles of cell wall acylation are unclear.

The goals of this project are to systemically characterize plant acyl-CoA dependent acyltransferases and acylases, therefore, to identify the specific enzymes involved in lignocellulosic acylation and deacylation, and further explore the underlying biochemical mechanisms and biological functions of lignocellulosic acylation.

APPROACH:

1) Biochemical genomics approach: We propose to identify all the putative acyltransferase and acylase genes from Arabidopsis and poplar genomes; followed by bioinformatics and transcriptional profiling analysis, we conduct comprehensive *in vitro* biochemical assay to systemically characterize the gene functions involved in cell wall biogenesis and modification.

2) Reverse genetics approach: As a complimentary approach, the corresponding Arabidopsis T-DNA insertion mutant lines will be screened and analyzed to detect the compositional changes of plant cell wall resulting from the deficiency of particular acyltransferase and/or acylase genes.

TECHNICAL PROGRESS AND RESULTS:

In the previous fiscal year (FY 2007), along with the synergistic support of LDRD and BER Plant Feedstock Genomics for Bioenergy Program Seed Fund, we have identified 94, and 61 putative acyl-CoA dependent acyltransferase genes from poplar and Arabidopsis, respectively, as well as 10 acylase genes from each species. To further probe gene expression pattern, the "*in silico*" transcription analysis and solid RT-PCR was conducted for all of the identified putative poplar genes by using RNAs prepared from poplar leaf, root, developing stem, apical bud, cortex of bark, phloem, developing wood and lignified wood. The studies led to the recognition of a number of acyl-CoA dependent *O*-acyltransferase and acylase genes that are preferentially expressed in secondary cell wall forming tissues (stem and xylem).

During FY 2008, we refined the bioinformatics and expression analyses on poplar and Arabidopsis acyltransferase genes. We revealed several unique features of acyltransferase family members for their gene structure, organization and distribution on genomes in both species; and we discovered a batch of tissue-specific and stress-inducible expressing genes. Those analyses afford a strong knowledge basis for understanding acyltransferase genes' evolutionary relationships, and the gene functions implicated in plant growth, development, and metabolism. We summarized our research data and submitted it to the journal *Plant Molecular Biology*, which was provisionally accepted for publication.

In FY 2008, we also performed comprehensive *in vitro* functional screening using the produced numbers of recombinant proteins for the putative poplar acyltransferases. This led us to characterize several novel functional enzymes, which include: (i) A novel monolignol acetyltransferase specifically responsible for the modification of lignin biosynthetic precursors, monolignols. The biochemical property and subcellular localization of this enzyme were further investigated. The correlation of the gene expression to the acetylation of cell wall lignin was explored and the transgenic plants were created. (ii) Two hydroxycinnamoyltransferases that displayed activities for synthesis of both monolignol biosynthetic intermediates and chlorogenic acid, a metabolite acting as phytoalexin in defense responses to phytopathogen. Overexpressing those genes in plant resulted in the large changes in lignin content, compositions, and xylem morphology.

In addition, we also characterized several novel aromatic acyltransferases responsible for modification of a variety of phenyl or aliphatic alcohols. Those identified genes will be useful molecular tools for re-directing photosynthetic carbons from lignin polymer biosynthesis into the value-added metabolites in plant feedstock.

In order to understand the molecular mechanism of cell wall acylesterification, we analyzed the wall-bound acylesters of poplar by using Liquid Chromatography-Mass Spectrometry (LC-MS), Fourier Transform-InfraRed (FT-IR) microspectroscopy, and synchrotron InfraRed (IR) imaging facility. The results revealed that the cell wall of dicotyledonous poplar, as the walls of many monocot grasses, contains a considerable amount of acylesters, primarily acetyl and *p*-hydroxycinnamoyl molecules. The "wall-bound" acetate and phenolics display a distinct tissue specific-, bending stress responsible-, and developmental-accumulation pattern, indicating distinct roles of different "wall-bound" acylesters in poplar cell wall structural construction and/or metabolism of cell wall matrix components. This study affords valuable information in understanding the physiological roles of cell wall modification and in guiding genetic manipulation of cell wall biomass to facilitating its conversion. This work was published in the journal *Planta* (2008).

Besides biochemical analysis, we also identified more than 60 Arabidopsis T-DNA insertion mutant lines of acyltransferases and we screened up to 40 homozygous lines. The chemical analysis on cell wall compositions of mutant will be performed.

Functional Neurochemistry

LDRD Project 07-048

Dardo G. Tomasi

PURPOSE:

Functional magnetic resonance imaging (fMRI), the method of choice for mapping brain function, is sensitive to unwanted contributions from large blood vessels, is not quantitative, and does not provide neuronal markers to study the dynamics of metabolic events during neuronal activation. Quantitative proton magnetic resonance spectroscopy (1H-MRS), on the other hand, can accurately determine metabolite concentrations and provides important information for the study of brain metabolism, which could validate fMRI measures and help in understanding brain function at the chemistry level. Thus, we aim to develop functional 1H-MRS (1H-fMRS) to measure metabolite changes during brain activation, a technique that could be a powerful tool to study synaptogenesis, neurogenesis, or processes involving structural changes in the brain.

APPROACH:

Brief as well as prolonged blocked visual stimulation will be used to induce measurable changes of metabolite concentrations in primary visual cortices, while fMRI and fMRS will be acquired in an interleaved fashion. Novel RF surface coils will be developed for improved MRS acquisition. Accurate spectral analysis, with increased sensitivity, will be developed for the detection of metabolic activation changes that cannot be determined in conventional fMRS approaches.

TECHNICAL PROGRESS AND RESULTS:

RF coil development: We continued the development of novel radiofrequency (RF) coils to increase the sensitivity to dynamic brain metabolic changes in our 4 Tesla MRI scanner. We also aim to improve the uniformity of the RF field in the occipital cortex in order to facilitate suppression of unwanted water signals during MRS. Specifically, during the 2008 Fiscal Year, we developed a novel quadrature transceiver RF surface coil that is based on two orthogonal RF slotted surface coils operating at 170 MHz in "L" configuration. Images acquired with this RF coil have 40% higher SNR ratio and better uniformity than the slotted surface coils we previously used for this project, making it ideal for magnetic resonance spectroscopy in the occipital lobe. Preliminary results obtained with this coil were presented in the Tenth Mexican Symposium on Medical Physics and were recently published (S.E. Solis, J.A. Hernandez, D. Tomasi, A.O. Rodriguez. "Two-slotted surface coil array for magnetic resonance imaging at 4 Tesla" *Med Phys* 1032: 152-154, 2008).

Data acquisition: We made significant efforts to improve the stability of the single-voxel PRESS pulse sequence with short echo time ($TE/TR = 30/2000$ ms) used to collect time series of water-suppressed MR spectra. Specifically, we performed a series of studies in phantoms to understand the origin of the fluctuation (10%) of the MRS signal phase, which seems to be associated to instabilities of the digital eddy current compensation (DECC) or the smart digital-to-analog conversion (SDAC) boards of the INOVA/Varian console. This hardware problem seems to be related to the aging (8 years of daily use) equipment, limiting our ability to detect small (< 5%) MRS signal changes as a function of time. This expensive (USD 800k) console is the heart of our MRI system and is not fully covered by the manufacturers' warranty, which covers

replacement parts but not the whole instrument (we replaced the suspicious boards but the problem remains).

Automatic LC data analysis method: We refined our automatic metabolite quantification software that is based on commercial software (LC) and a spectra database of brain metabolites at 4-Tesla magnetic field. Specifically, we developed a user friendly suite of interacting subroutines written in Matlab language that allows the user to determine time-varying metabolite concentrations from MRS time series.

Stimulation paradigms: While using flickering checkerboard paradigms, we were able to reliably activate the human occipital visual system. We were unable to produce reliable modulations of brain metabolites in the brain. This problem could be related to the phase instabilities mentioned in “Data acquisition” but could also reflect a not strong enough visual stimulation because subjects that participated in the study rated the flickering checkerboard paradigm as “boring”. Thus, we decided to use movie trailers as visual stimuli instead of the long and boring checkerboard paradigm because these action movies that strongly engage the visual system were rated as “exciting”. We developed software in Visual Basic and Visual C++ to display the movie trailer stimuli to the subjects’ eyes on MRI-compatible LCD goggles connected to a personal computer. To allow time-locked 1H-MRS techniques, this software synchronizes the stimuli with the fMRI/fMRS acquisition by using a trigger signal from MRI console. As before, the brief (3 minutes) stimulation paradigm has a 30-seconds flickering (5-Hz) checkerboard vs. 30-seconds baseline (black screen) blocked design. The new prolonged visual stimulation uses 12-minute long action video trailers. To determine if with the new stimulation paradigm and the novel RF coil we can detect dynamic brain metabolite changes in the occipital cortex we will collect preliminary data in ten healthy volunteers during the winter. As before the fMRI scan will be done first and the corresponding activation pattern was used to identify activated occipital regions stimulated by the 5-Hz flickering checkerboard paradigm and we will plan the location and size of MRS voxels. The MRS data was fitted to our spectra database, accounting for concomitant BOLD-related time-varying changes in local magnetic susceptibility during activation. We hope that with this approach we will be able to produce significantly higher brain metabolite changes that allows us to overcome the hardware-related phase instability threshold (5%) of our MRI system.

Miniaturized RF Coil Arrays for MicroMRI

LDRD Project 07-054

S. David Smith

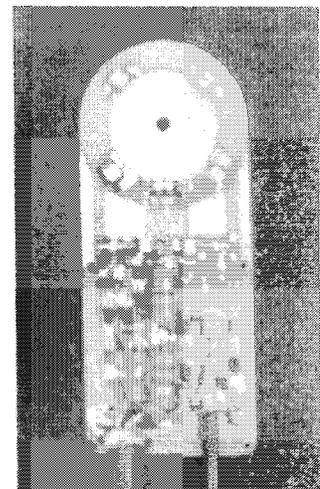
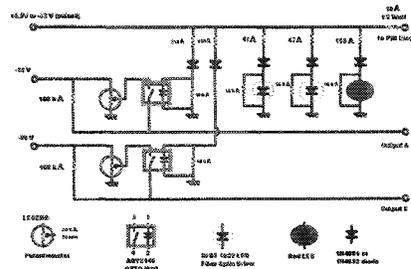
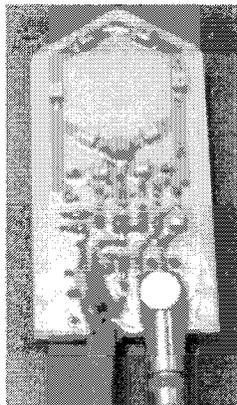
PURPOSE:

Our project's goal is the development of novel, high performance radio frequency (RF) coil arrays for improved imaging on the Medical Department's 9.4 Tesla (400 mhz) micro MRI system. We designed and built several coil arrays, specifically for use in the 'parallel imaging' mode. The greatest challenge in designing array coils for high field small animal MRI systems, is in the fabrication of the *highly miniaturized* RF coil arrays that are fully integrated with their associated electronics. Independent receiver chains and tuning circuitry are required for each coil element and maximum performance can be achieved only if the early stages of the receiver chains, such as the tuning circuitry and signal pre-amplifiers are incorporated into the construction of the coil array itself. Coil arrays, when used in the parallel imaging mode, can dramatically improve imaging performance in terms of increased signal to noise ratio (SNR), reduced image acquisition time and image coverage. The benefits provided by array coils are based on the fact that smaller coils will provide a better sensitivity (i.e. increased SNR) over a smaller imaging volume or "field of view" (FOV). The reduced field overlapping views of the multiple coils are then combined into a single image, providing further benefits of increased FOV, SNR and acquisition speed. Realization of the goal of providing increased SNR will benefit every aspect of the Medical Department's Micro MR Imaging research program, yielding the same increased performance as might be obtained in a much more costly fashion by upgrading to a higher magnetic field strength.

APPROACH:

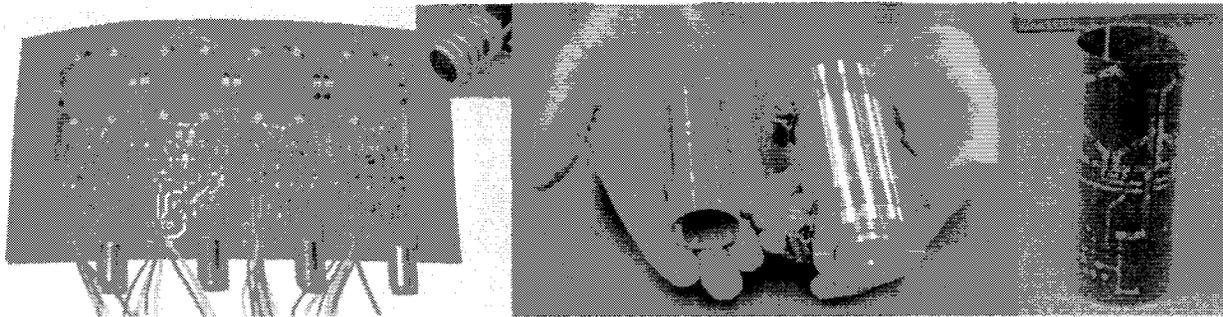
Parallel imaging is the recently developed technique, widely applied in the most advanced commercial clinical MRI systems. Comparable devices are not yet commercially available for small animal Micro MR imaging systems. MicroMRI applications need reduced imaging volumes for small animal subjects, vis a vis, clinical MRI applications. The small size of the imaging volume leads to more difficult requirements for miniaturizing and more exacting tolerances in coil construction and assembly. Expertise in these areas is being provided through collaboration with the Central Shops' Tom Lambertson, William Lenz of the Physics Department and the Instrumentation Division's Sergio Rescia.

TECHNICAL PROGRESS AND RESULTS:



The research focus in the first half of fiscal 2008 completed single coil design and component evaluations begun in FY 2007. The basic single coil design shown in the upper left hand corner of the figure above, together with the modified detuning circuitry described in the schematic has been shown to give superior performance to that of the original coil provided with our 9.4 Tesla MR Spectrometer system by the manufacturer. It is now being used for all MR imaging and MR spectroscopy studies at our microMRI Laboratory. Further reductions in size can be accomplished upon the receipt of components currently on order. We have planned fabrication coils at $\frac{1}{2}$ and $\frac{1}{4}$ scale to the present design.

During the second half of the FY2008, efforts centered upon the development of fabrication techniques for making coils arrays with *precisely* controlled geometrical relationships amongst coil elements. Printed circuit techniques allow for exacting geometrical specification on a two dimensional surface. In order to extend this precision to a three dimensional space, we developed a lamination technique which forms the *planar* printed circuit layout into a cylindrical array. Components can then be mounted on the outside of the cylinder. This technique maintains the full precision of the printed circuit layout, while providing sufficient structural rigidity to ensure that intra coil couplings (mutual inductances) are stable and measurable.



Neurocomputation at BCTN: Developing Novel Computational Techniques to Study Brain Function in Health and Disease

LDRD Project 07-055

Rita Goldstein, Nelly Alia-Klein, Dardo Tomasi, Dimitris Samaras and Joanna S. Fowler

PURPOSE:

The Brookhaven Center for Translational Neuroimaging (BCTN) houses three important tools for in vivo brain imaging: positron emission tomography (PET), functional magnetic resonance imaging (fMRI) and event-related potentials (ERP). The BCTN also acquires the functional assessment of cognitive brain processes with neuropsychological (NP) examinations. The present project is a cutting-edge effort at both the conceptual and computational levels to model and study the human brain in health and disease through the integrative use of these multiple data sets. This effort, therefore, furthers the central role of the BCTN as a meaningful integrator of multiple data sets (all from dynamically changing biological systems) toward current DOE initiatives of establishing BNL as a leader in the fields of Brain Health and Computational Biology.

APPROACH:

The current proposal bridges PET, fMRI, ERP and NP technologies to develop a state-of-the-art neurocomputational platform supporting multi-dimensional computational analysis of the human brain (chemical, metabolic, anatomical and psychologically functional). In our analyses, we resolve incompatibilities between PET, fMRI and ERP acquisitions (note different time scale from minutes, to second, to milliseconds, respectively); and use the newly emerging field of neurocomputation to set these multiple measures into a common database that allows the valid modeling of brain function. Our NP models guide the questions we pose.

TECHNICAL PROGRESS AND RESULTS:

An integrated source for multiple datasets: We have been consolidating all datasets inside a flexible, well-supported and extendable database for each human subject. This work in progress requires the capture of a multitude of data fields acquired during each procedural encounter. Data entry tools have been written which enforce error-checking and facilitate specialized and compartmented control of data entry stored directly to the database. The populated neurocomputational database is assembling records vectored across domain fields and now supports a growing set of user-definable queries. A mapping key strategy for uniquely identifying related records across NP, fMRI, ERP, and PET domains has been validated as a clear and robust linking mechanism and has been incorporated to relate subject records from the variety of protocol encounter collections across all data tables. Automated mapping key generation has been implemented inside our existing fMRI and NP protocol records, and supports the automated linking and expedited import of data into the neurocomputational network.

Combined fMRI-ERP developments: To further the consolidation of fMRI and ERPs, Muhammad Parvaz, our Ph.D. student from SBU Biomedical Engineering Department, has attended a highly competitive 2-week workshop on combining fMRI and electrophysiological recordings at UCLA. He is now integrating ERP source analysis mapping with separately acquired fMRI activations, and preparing for simultaneous fMRI-ERP acquisitions with the development of two computerized behavioral tasks applicable for separate ERP and fMRI stimulation, which will become a base for bridging analyses of both datasets. His work has been

featured in the press book of the Society of Neuroscience 2007 annual meeting. This work is now in further development with a newly established collaboration with SUNY SB's Greg Hajcak, Ph.D., and expert in ERP studies; an abstract based on this work has been presented in the 48th Annual Meeting of the Society for Psychophysiological Research in Austin, TX, Oct 2008 and a journal manuscript is now in its final stages of preparation.

Combined fMRI-PET developments: Samuel Asensio, a graduate student from Valencia, Spain, integrated dopamine receptor availability PET data with our fMRI results to answer the first question that we posed in our original application: "Are impairments in immediate and sustained responses to monetary reward driven by decreased levels of dopamine?" A manuscript based on these results has now been submitted for peer-review. To further this question we have integrated the fMRI study administration of methylphenidate, a dopamine agonist. We have received IRB approval for implementation of this pharmacological intervention and collected drug and placebo fMRI data from control (8) and cocaine addicted (4 plus 10 pilot) subjects. We plan to integrate into our studies treatment approaches based on our current results (e.g., NP exercises for brain regions known to be implicated in drug addiction; and enhancement of the brain regions underlying inhibitory control by other methodologies, including repeated transcranial magnetic stimulation to decrease craving and enhance inhibitory control).

NP task development (to equalize acquisition across modalities): We are continuing to develop new tasks designed for application across imaging modalities and to enable task-synchronized analyses. For example, we have been adapting the PET developed cocaine videos to the fMRI environment, and a new collaboration with Uri Hasson of NYU, an expert in this specific data analysis for fMRI (real-time complex intercorrelational datasets), has been established to further this goal. In addition, Scott Moeller, a Ph.D. student at Univ. of Michigan, has worked with us for the past two years to develop additional tasks that tap into objective measures of reward processing and decision making in an emotional context. The results have now been presented at SFN, featured in the press book of the Society of Neuroscience 2008 annual meeting, and are currently under review.

Computer Science Applications: We have recruited three graduate students from the SBU Computer Science Department: Alex Panagopolous, Jean Honorio Carillo and Juntian Shan. These students are validating and extending the data-driven algorithms developed by our previous computer science student, Lei Zhang, Ph.D., which demonstrated highly sensitive and selective discriminations between fMRI responses to reward in subjects with and without histories of addiction. This pattern recognition discrimination software is now being validated across other tasks, imaging modalities, and samples of drug addicted individuals; it is also being assessed in more brain regions and studied for further optimization of the classifier network parameters. Together, these efforts help us answer the second question in this proposal "What are the neural features that best discriminate cocaine users from non-users when processing reward?" Moreover, we have been establishing a working collaboration with Georg Langs, of MAS laboratory at Ecole Centrale de Paris, and Hava Siegelmann of University of Massachusetts, to further the use of computer science algorithms for data integration and higher-order analyses. First applications focus on utilizing the temporal dynamics and neural network approaches together with machine-learning modeling of the data. We also use facial discrimination algorithms developed by Dimitris Samaras, our computer science USB collaborator, to automatically and objectively identify craving. This will have a high impact in the field of drug

addiction (and other disorders of uncontrollable behavior) as to date craving has only been identified using self-report. Our objective algorithms will increase prediction of treatment outcome measures such as drug abuse and relapse while offering a cutting-edge scientific tool to identify, diagnose and predict hitherto subjective human emotions.

A Non-Fermentation Route to Convert Biomass to Bioalcohols

LDRD Project 07-059

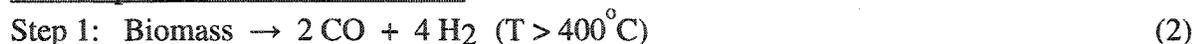
Devinder Mahajan

PURPOSE:

In the commercial biomass fermentation route, ethanol-producing microorganisms only utilize C-5 and C-6 sugars leaving other complex molecules unconverted and produce 2 moles of undesirable CO₂, wasting 2 carbon atoms in feedstock (equation 1). The alternate "Thermochemical route", is a two-step process through which biomass from a variety of sources can be converted into useful fuels and chemicals. In the latter route, the first step is biomass depolymerization via gasification to yield synthesis gas (or syngas), primarily a mixture of CO and H₂ (equation 2). The second step follows with conversion of syngas into ethanol with Rh-based catalysts (equation 3) though total carbon utility remains a challenge due to production of unwanted side products such as methane.



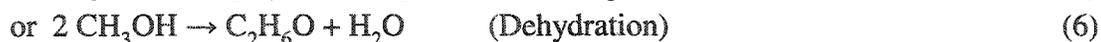
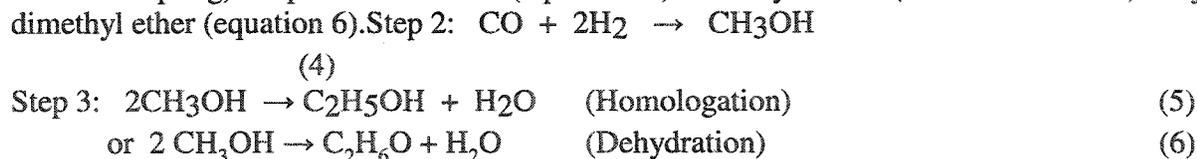
Two-step "Thermochemical" Route:



Our focus is on designing highly active catalysts that: 1) operate in aqueous media, 2) can efficiently convert syngas into ethanol under low temperature/pressure conditions. The objective of this research aligns with the BNL strategic goal to synthesize biofuels. A successful proof-of-concept will lead to new technologies for synthesis of higher alcohols and/or other oxygenates that are of interest as commercial transportation fuels.

APPROACH:

The literature studies show that Rh-based systems are the catalyst of choice for ethanol production vis equation 3. However, ethanol yield are low due to poor selectivity at temperatures > 200°C and copious amount of undesirable methane is also produced. Our proposed approach envisions efficient methanol synthesis (equation 4). Methanol can then undergo homologation (carbon-carbon coupling) to produce ethanol (equation 5) or dehydration (C-O-C formation) to yield dimethyl ether (equation 6).

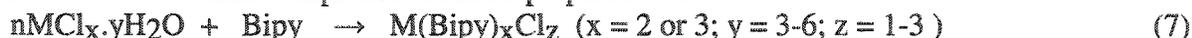


A typical experiment was conducted as follows. A Parr batch unit consisting of a 300 mL pressure vessel was utilized for catalyst screening studies. The unit was fitted with ports for gas/liquid inlets, liquid/gas sampling valves, rupture disc and other safety devices. Each run involved mixing 1 mmol catalyst, 100 mL methanol and 0.1 mol base (if added) in the vessel and pressuring with 300 psig N₂ (inert) gas. The vessel was heated after sealing and any pressure change was recorded. The reactant/product were analyzed before/after heating to identify products produced. In addition to gas chromatographs, infrared spectroscopy was used to confirm products. Since dimethyl ether (DME) is a gas at room temperature (b. pt.: -23°C), its production was qualitatively monitored by observing increased pressure of the system under reaction conditions.

The work was coordinated with Drs. K. Ro and P. Hunt from the Agriculture Research Service-United States Department of Agriculture (ARS-USDA), Florence, South Carolina facility for application to syngas produced from animal waste.

TECHNICAL PROGRESS AND RESULTS:

In FY 07, two tasks were completed. First, synthesis of water-soluble metal complexes was developed. This involved refluxing metal chloride with a basic ligand (2,2'-Bipyridyl or Bipy) in methanol/water solvent for 15 minutes, followed by cooling to yield yellow or green crystalline compounds, depending on the metal used (M = Rh, Ru, Ni; Ligand/M = 1/1 or 2/1). The synthesized complexes were characterized via infrared and elemental analysis. However, it was found that the same complexes could be prepared *in situ*.



The second task was to evaluate these catalysts for methanol conversion to higher oxygenates via equations 5 or 6. Two catalysts, Rhodium on alumina (Rh/Al₂O₃) and triruthenium dodecacarbonyl (Ru₃(CO)₁₂) were screened at 150° and 200°C. No reaction occurred at 150°C but at 200°C, reaction 6 dominated to produce dimethyl ether (DME) and only trace ethanol was quantified. The activity followed the order: Ru (5.9%) > Rh (2.9%) where the values in parenthesis are DME volume % in the collected liquid after the reaction.

In FY 08, the focus was to maximize DME production since this molecule is considered a replacement for diesel. A total of 15 runs were conducted with full mass balance to compare activities of metals less expensive than Ru for DME synthesis. These were: Cobalt chloride (CoCl₂) and Nickel chloride (NiCl₂). The total reaction time was typically 6.5 hours at 200°C, and DME was found in both liquid and vapor phases using CoCl₂ and NiCl₂ catalysts. The system pressure increase was between 12 - 155 psi indicating the change from methanol to DME. A series of runs with NiCl₂ yielded maximum DME as 6.6 vol. %, the rest of liquid being unreacted methanol. The gas phase consisted of 52.3% H₂ and no CH₄ was produced. A series of runs with CoCl₂ yielded maximum DME at 8.8% in the liquid phase. The corresponding H₂ in the gas phase was 38.8% and CH₄ production was low (< 0.5%). The data gathered from the batch runs showed that: 1) added base (KOH) increased DME production: CoCl₂ (3.11%) vs CoCl₂/KOH (8.7%), 2) increasing reaction temperature decreased reaction time for the CoCl₂/KOH system: 250°C (1.5 h) vs 200°C (6.5 h) and 3) CoCl₂ was more effective for DME production: CoCl₂ (8.7%) vs NiCl₂ (5.6%). Neither Ru₃(CO)₁₂ nor CoCl₂ catalysts were able to synthesize ethanol, showing methanol homologation was not preferred under the moderate reaction conditions. The co-production of DME and H₂ is of interest. H₂ is likely first produced by methanol decomposition and then it is augmented by water-gas-shift reaction. The absence of CO₂ in the product is due to its reaction with the base. Results also show that with NiCl₂, the product shifted from DME to ethanol (8.47 vol%) by increasing the temperature from 200°C to 250°C, suggesting a change of reaction pathway from dehydration to homologation.

In FY 09, the work is focused on maximizing DME and ethanol with Co and Ni catalysts, respectively. The concept is also being applied to syngas from animal waste and glycerol for conversion into oxygenated fuels.

Fate and Reactivity of Carbon Nanoparticles (CNPs) Exposed to Aqueous Environmental Conditions

LDRD Project 07-062

Barbara Panessa-Warren and Kenya Crosson

PURPOSE: Carbon nanoparticles are currently widely used in research, industry and commercial products, both in the United States and globally. These nanoparticles can find their way into our soil and water environment following product use, disposal and degradation, yet it is not known if the presence of these nanoparticles, pose any threat to the environment or human health. The purpose of this investigation was to compare the (1) fate and reactivity of single walled carbon nanotubes (SWCNTs) following aqueous exposure saline and fresh (~18M Ω) water (at neutral to alkaline pH) over time (0-7 yrs); and (2) whether SWCNT cytotoxicity to human cells was ameliorated following extended aqueous exposure. This study answered the questions:

1. Are physico-chemical characteristics of SWCNTs altered following controlled aqueous exposure in fresh and saline water?
2. What characteristics of the SWCNTs were associated with human cell cytotoxicity, and whether cytotoxicity was ameliorated following saline or fresh water aqueous aging?
3. Can this information be used to develop safer handling, storage and disposal of SWCNTs making them non-reactive in aqueous environments and in the presence of human cells?

Follow-on Implications: The data from this LDRD will form the basis for proposals to Homeland Security, and the DOD involving strategies for detoxifying carbon nanoparticle contaminated environments, and Dr. Crosson will pursue a grant proposal to NSF and an EPA/NSF &UK proposal on fate and reactivity of nanoparticles in the environment. A DOE proposal is also planned for the development of a carbon nanotube laser detector system.

APPROACH:

Fullerenes aggregate following aqueous exposure to saline and natural organic matter (NOM)^{1,2}, which indicated that the components in natural water (humic & fulvic acids and NOM) could bind to carbon nanoparticles producing large nanoparticle aggregates which would be less environmentally reactive. Similarly, SWCNTs were found to form micrometer sized aggregates in experimental aqueous environments³, but aggregate characteristics changed depending on post synthesis treatments utilized in industrial processing (e.g. acid cleaning)⁴.

In our investigation, we determined how SWCNT characteristics (aggregation, reactive groups, lack of metal catalyst, morphology) changed following aqueous exposure, and whether these changes in SWCNT characteristics altered interactions with human cells. This provided new information on SWCNTs in aqueous environments, and what implications this has for human health and safety. For this study Dr. Panessa-Warren had stored, acid cleaned, and 'as prepared', SWCNTs suspended in phosphate buffered saline (PBS) or ~18 M Ω fresh water, in sealed vials, as well as the original batch of 'as prepared' SWCNTs. These samples had been stored for 0.7 to 7.0 years, permitting us to study long term nanotube aqueous exposure.

Scope of the investigation: This project was divided into two separate thrusts: A. The physico-chemical analysis of SWCNTs in their 'as prepared' (from the manufacturer), and following acid cleaning (to replicate the commercially prepared nanoparticles used in manufacturing); and

B. Cytotoxicity testing of each type of SWCNT with human cell monolayers. Monolayers were prepared for viability staining, SEM and TEM imaging to evaluate cell viability, ultrastructural cellular morphology (interactions with nanotubes and aggregates) and attachment of nanotubes to the cell surfaces.

TECHNICAL PROGRESS AND RESULTS: 'As prepared' Carbolex and acid cleaned Carbolex SWCNTs incubated with human lung epithelium showed significant cell death following 3 hr exposure to freshly made solutions regardless of metal catalyst content. However following 2.5 yr exposure to pH neutral saline, the same nanotube solutions showed markedly less toxicity approaching normal cell values. However acid/peroxide (A/P) cleaned nanotubes caused high cell death regardless of years of aging in ultrapure water (Fig.1A), whereas when the same A/P CNTs were bathed in saline (S), or natural organic matter (NOM) found in river and fresh natural waters, [for 90 or 120 days] the toxicity of the A/P CNT was significantly reduced (Fig.1B). Microscopy studies showed severe membrane damage to cell monolayers following A/P CNT incubation (Fig.2A, arrows-nanotube aggregates), but virtually no surface membrane damage to cells exposed to the same A/P CNTs suspended in PBS saline (Fig.3C,D arrow-nanotube aggregate) or NOM (Fig.3E granular material is aggregate). Similar results were seen with human colon cells. Physico-chemical analyses done by Dr. Crosson indicated a greater presence of hydroxyl, carboxyl and alkyl functional groups following extended exposure of 'as prepared' SWCNTs stored 45 days in ultrapure water. Similarly, exposure to NaCl and alkaline (pH 8,10) waters increased surface hydroxyl groups (seen by FTIR) on as prepared SWCNTs.

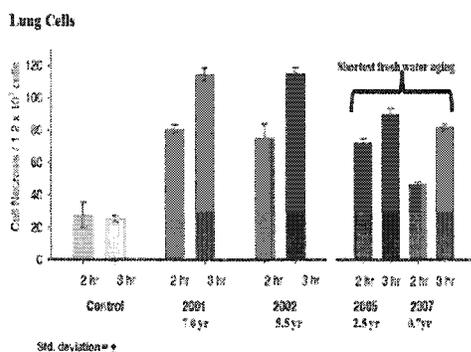


Fig.1A.

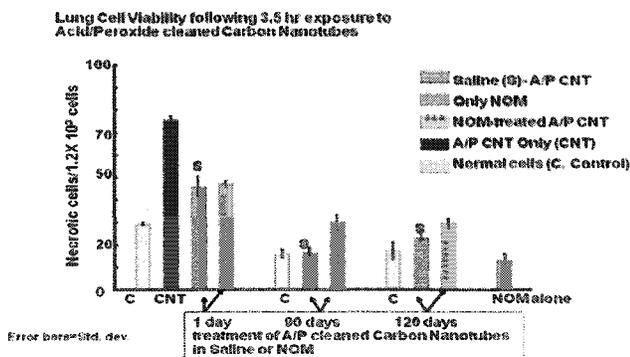


Fig.1B.

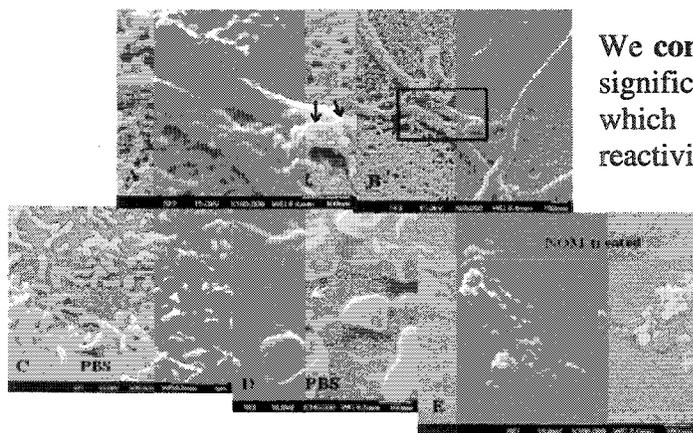


Fig.2.

We **conclude** that SWCNT surface chemistry can significantly change in aqueous environments, which can be exploited to control toxicity and reactivity, and insure human health and safety.

1. Brant et al. 2005, J. Nanopart. Res. 7:545.
2. Lecoanet et al. 2004, *Envir. Sci. & Tech* 38: 5164.
3. Cheng and Cheng, 2005, *Off. J. Soc. Toxicol.* 84:9.
4. Chen et al. 2004, *J. Colloid Interface Sci.* 280:91.

Development of Room-Temperature CdMnTe Gamma-Ray Detectors

LDRD Project 07-073

Yonggang Cui

PURPOSE:

The goal of this project is to develop new room-temperature gamma-ray detectors based on CdMnTe (CMT) crystals. Its wide band-gap, high resistivity, and good electron-transport properties make it a viable candidate for detecting gamma rays. In addition, its relatively low-temperature growing process ensures good compositional uniformity and fewer impurities, potentially resulting in a high yield of the crystals in making detectors and large-area detector arrays.

In this project, we investigated the required characteristics for CMT as a material for gamma-ray detectors. The success of this work led to increased knowledge of the crystals for radiation-detection applications and new results for CMT's properties and their relationships to device response.

APPROACH:

CMT crystals have been proposed as potential gamma-ray detectors. Mycielski *et al.* (2005) discussed the current state-of-the-art of CMT crystals specifically grown for nuclear-detector applications. Indium (at $\sim 10^{17} \text{ cm}^{-3}$)-doped $\text{Cd}_{0.87}\text{Mn}_{0.13}\text{Te}$ crystals grown at the Institute of Physics, PSA (Warsaw, Poland) exhibited resistivity and mu-tau products exceeding $10^{10} \Omega\text{-cm}$ and $10^{-5} \text{ cm}^2/\text{V}$, respectively. These crystals were used to fabricate devices that could detect 5.5-MeV alpha particles from an ^{241}Am source, and gamma radiation from ^{241}Am and ^{57}Co sources. The present electron mu-tau value of $\text{Cd}_{0.87}\text{Mn}_{0.13}\text{Te}$ detectors ($\sim 10^{-5} \text{ cm}^2/\text{V}$) is too small to assure good spectral performance for long drift-length detectors. This project seeks to improve the transport properties of CMT materials to produce a new class of solid-state gamma detectors for spectroscopy and imaging.

In this project, we collaborated with PAS on crystal growing. Dr. Mycielski grew CMT ingots. All the CMT samples were tested at BNL, and the results were fed back to PAS for improving the crystal growing process. We repeated this loop to accomplish higher resistivity, higher mobility-lifetime product, and lower defect density crystal growth methods.

For each CMT sample, we proceeded with the crystal polishing first, followed by IR measurement to investigate the Te inclusions in the bulk of crystals, and I-V curve measurement to select high resistivity sample. For the high resistivity samples, we developed contacts on the surfaces using an electroless gold method. In addition to characterizing and testing these detectors with sealed sources, we also used x-ray beams at NSLS to characterize the electrical-, structural-, and transport- properties of CMT on a micron scale. These properties were correlated with other material properties to understand nonuniformities and improve surface preparation processes.

We also did EPD (etch pit density) measurements on CMT samples. This measurement helps us identify the defects that are invisible under infrared light. It is a complementary approach for understanding the material properties of CMT samples and the spectral response of CMT detectors.

Other investigators involving in this project include A. Hossain and P. Vanier.

TECHNICAL PROGRESS AND RESULTS:

In FY2008 year, we characterized more than 30 samples from CMT ingots that were grown in different conditions. A few high resistivity samples were selected and fabricated into CMT planar detectors.

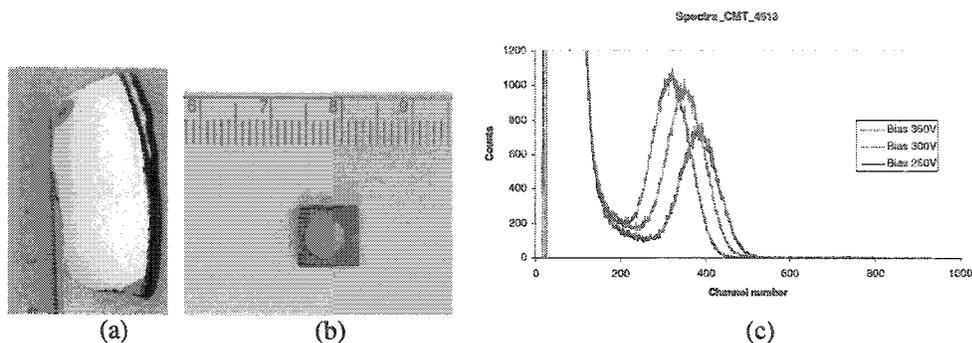


Fig. 1. CMT detector. (a) wafer cut from CMT ingot; (b) planar CMT detector; (c) spectral response of a CMT detector.

In FY2008, EPD measurements were well established in our lab with support from this LDRD project. This powerful experimental approach allowed us to identify the extended defects in crystals. Some of these defects couldn't be seen using infrared transmission measurements. EPD images in Fig. 2 show the variation of etch-pit density in different areas of a wafer.

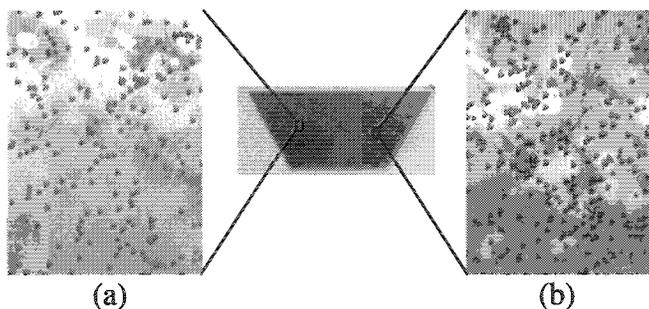


Fig. 2. EPD measurement results on a CMT sample. (a) area close to the center of ingot; (b) area close to the crucible wall.

In addition, we also conducted research on the effects of chemical etching on the surface roughness of CMT crystals. This is an important research to select the best chemical etching method for detector fabrication. Fig. 3 shows our test results. Detailed results were published at the SPIE 2008 conference.

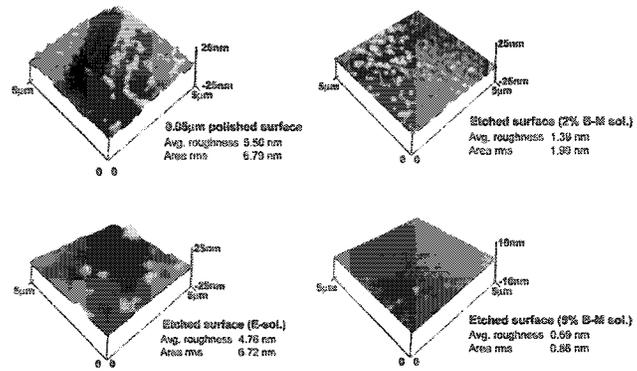


Fig. 3. Effects of chemical etching on the surface roughness using different etchants.

Developing a New Framework for Investigating Earth's Climate and Climate Change

LDRD Project 07-075

Yangang Liu

PURPOSE:

The overarching goal is to develop a new framework for studying Earth's climate and climate change, with two major objectives. The first objective is to examine the role of entropy (budget) in shaping Earth's climate and its change. The second objective is to seek simple guiding principles that govern Earth's climate as a whole without knowing the "microscopic" details. The two objectives are complementary to each other as the state of a large system is likely constrained by entropy-related principles such as maximum entropy principle for equilibrium systems, minimum entropy production principle for near-equilibrium systems, and maximum entropy production principle for systems far-from equilibrium. This work will shed new light on many crucial issues regarding Earth's climate and climate change, and enhance our ability to predict them. Specifically, the work will lead to improved quantification of the role of entropy in shaping Earth's climate and new understanding of climate forcings from aerosols and greenhouse gases. The success of this work will give BNL an edge in competing for funding in ongoing and future programs (e.g., ARM, ASP, CCPP and SciDac) because understanding and modeling Earth's climate and human induced climate change is a central part of the DOE science mission. The results from this proposal will also find additional applications in studies of complex systems (e.g., ecological and biological systems) in general. The proposed task is directly tied to the BNL strategic areas of climate sciences, computational sciences, and basic and applied sciences, and indirectly related to that of energy sciences.

APPROACH:

Climate involves (infinitely) many interacting subsystems that themselves consist of ever smaller units, and a proper theoretical framework is central for virtually all climate-related scientific issues targeted by the DOE mission. Despite of its successes over the last few decades, the current mainstream framework suffers from two major deficiencies. First, current climate studies center on the concept of energy but overlook entropy, especially in studies of climate change. This neglect of entropy is problematic because any change of a system is related to entropy no less than to energy. Second, current climate models such as general circulation models are built upon the idea of breaking down Earth's system into ever-smaller interacting subsystems, which, in a sense, is like trying to describe the behavior of a gas by tracking every molecule. Despite the advantages of being able to have detailed investigation into individual processes, accurate representation of increasingly detailed subsystems, their interactions/feedbacks, along with the increasingly high demand for computer resources, poses both theoretical and practical challenges to such reductionism approach.

A major thrust of this proposal is its focus on entropy and entropy-related principles (e.g. second law of thermodynamics for nonequilibrium systems) in addition to energy (budget). Theoretical studies, model simulations, and analysis of both observational data and model simulations will be carried out in parallel to achieve the objectives. Theoretical studies will start with a simple system, and gradually increase the level of model complexities. I intend to use the analogy with thermodynamics and statistical mechanics and take advantages of the development in these fields to explore the new theoretical framework. Theoretical analysis can be used to assist examination

of data from observations or model simulations. A major motivation to analyze model simulations is to discern the model problems and to determine if the problems are related to the neglect of entropy-related issues.

TECHNICAL PROGRESS AND RESULTS:

In this fiscal year, progresses have been made on four fronts. First, we have examined the concept and theory on radiation entropy, reviewed approaches for calculating the Earth's radiation entropy flux and formulated new ones. The Earth's radiation entropy fluxes were calculated using different expressions; errors and underlying physics were analyzed. Figure 1 shows that the differences of the Earth's radiation entropy fluxes calculated from different expressions are substantial, larger than the largest term of Earth's entropy generation ($0.298 \text{ W m}^{-2} \text{ K}^{-1}$). This work clarifies long-standing confusions in radiation entropy calculations, and has potential application to understanding the Earth's climate. A paper was submitted to *Review of Geophysics* for publication. Second, a new theory has been formulated that provides a physical explanation for the outstanding puzzle of why the observed shortwave planetary albedo tends to be around 0.3. As a part of this theory, a new expression is established that relates the Earth's effective longwave emissivity to the atmospheric emissivity and the surface emissivity for the first time. A paper is being prepared for publication in *Nature*. Third, a new global mean one-dimensional climate model has been established, and applied to investigate entropy and energy constraints using the new expression derived in the first task. Finally, an entirely new model has been explored by generalizing the effective emissivity expression to consider atmospheric temperatures as well. We are in a process of comparing the two 1D models, and preliminary results indicate that these entropy-related models can help solve the long-standing puzzle of if and how atmospheric convection such as clouds regulates Earth's climate. Two papers are being written to report the models and results for the special issue of the Philosophical Transactions B, Maximum Entropy Production in Ecological and Environmental Systems.

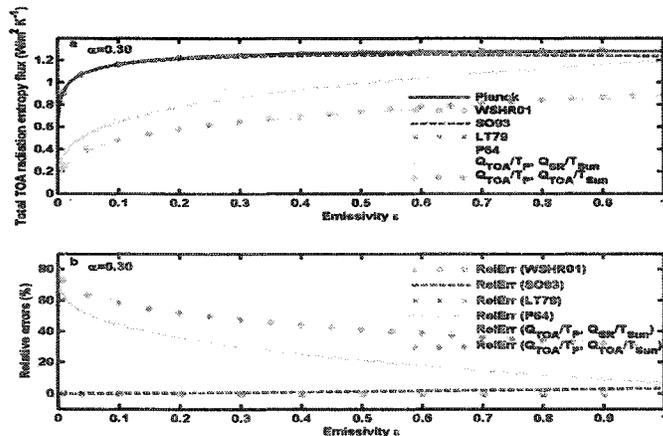


Figure 1. a) The Earth's TOA radiation entropy flux; b) Relative errors to Planck's expression.

A Novel Approach for Efficient Biofuel Generation

LDRD Project 07-080

Dev Chidambaram

PURPOSE:

The objective of this work is to create a functionally-bioactive microorganism encapsulated polymer fiber material for the first time. Traditional methods of immobilizing microbes have not had much success in terms of survival rates of immobilized bacteria. One of the drawbacks has been the solid nature of materials used; solid materials provide bacteria with no channels for respiration or for obtaining nutrients. Our results are encouraging and demonstrate the need for continued research in the development of such microbially active materials.

APPROACH:

Although microorganisms have been used in industrial and niche application for ages, successful immobilization of microbes while preserving the desired functionality has been elusive. This work aims to create polymer fibers containing bacteria, for the first time, through a novel process that allows the formation of pores on the fibers. These pores allow the microorganisms to respire. Application for such a functionally bioactive material ranges from biosensors, biofuel cells, environmental remediation, ground water decontamination, biocatalysis and is only limited by imagination. In short, these biohybrid materials can act as living membranes.

The multistep approach consists of starting from simple polymers and slowly increasing the complexity of the system to attain the bioactive fibrous material and is outlined as follows:

- (i) create fibers of a biocompatible polymer (for compatibility with microbes)
- (ii) encapsulate microorganisms in these fibers
- (iii) test the viability of these microorganisms
- (iv) modify process conditions to increase the density of the microbes in the fibers
- (v) identify optimal conditions to attain high microbial density and viability for required use

The bioactive material is produced by Y. Liu, a graduate student working on this project under the mentorship of the PI and Prof. M. Rafailovich of Stony Brook University. Prof. Rafailovich is a collaborator on this project.

TECHNICAL PROGRESS AND RESULTS:

In the last technical report (FY07), we described using a blend of polymers to create a biocompatible mat of filaments. These fibers were stable and the process conditions were optimized to create filaments, over 95% of which were in the preferred 500-1000nm range. The polymer blend was then used to successfully immobilize microorganisms. While the material was water soluble, a major shortcoming, this was nevertheless a major technical milestone.

In FY08, we studied the viability of the microbes in the fibers immediately after creation and with time. We have identified process conditions to create these materials, which allow the microorganisms to survive for a week in a refrigerator at 4°C (Fig 1). Furthermore, the materials can be successfully stored at -70°C for several months.

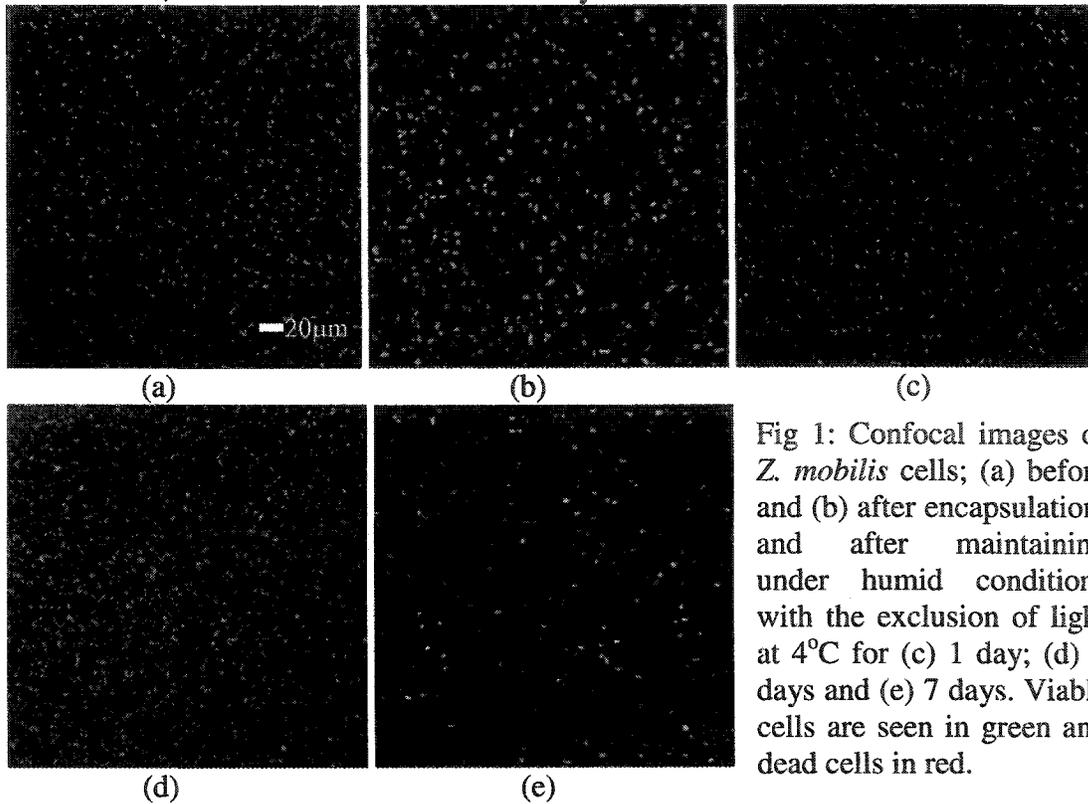


Fig 1: Confocal images of *Z. mobilis* cells; (a) before and (b) after encapsulation; and after maintaining under humid conditions with the exclusion of light at 4°C for (c) 1 day; (d) 3 days and (e) 7 days. Viable cells are seen in green and dead cells in red.

Also, we have created the next generation bioactive material, one that is water insoluble, via post-creation treatment of the fibers. These lead to insoluble material with viable microorganisms as shown below in Fig 2.

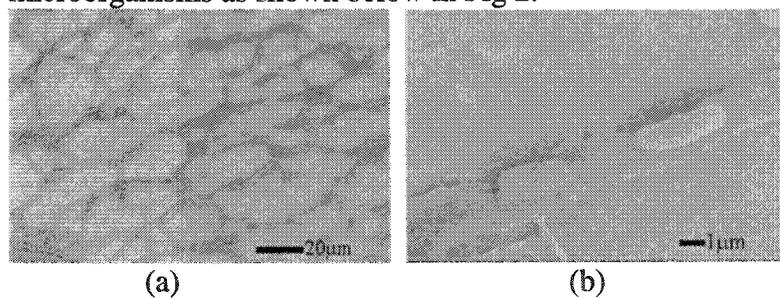


Fig 2: SEM images of insoluble bioactive material showing (a) a fibrous networked bulk structure and (b) a magnified image showing encapsulated microbes

Summary:

We have created, to our knowledge, the first insoluble microbially active polymeric material. The microbes were remained viable for several months.

In the current FY, we are working to optimize the process to yield the highest density of encapsulated microorganisms and to study their functionality. Further, we are determining whether the process can be utilized with other ubiquitous microorganisms.

Investigations of Hygroscopic Growth and Phase Transitions of Atmospheric Particles by Noncontact Atomic Force Microscopy

LDRD Project 07-084

S. E. Schwartz and A. Checco

PURPOSE

The effects of aerosol particles (nanometer to micrometer sized particles suspended in air) on atmospheric radiation and cloud microphysics need to be understood and represented in climate models to accurately represent climate change over the industrial period and future climate change that would result from future changes in atmospheric composition. Uncertainty in the magnitudes of these effects is the major contributor to uncertainty in radiative forcing over the industrial period. Reduction of these uncertainties requires better fundamental understanding of two processes: “aging” (by which non-hygroscopic particles become hygroscopic) and deliquescence (by which hygroscopic aerosols take up water and eventually become liquid), both of which affect aerosol light scattering and influences on clouds and precipitation. *The objective of this LDRD is to show that Atomic Force Microscopy (AFM) can improve the understanding of these processes on the nanometer scale.* Unlike methods that measure the average properties of an ensemble of aerosol particles, AFM allows detailed observation of changes of single particles. This work will thus provide insight into the physics of phase transitions at the nanometer scale and will contribute to improved representation of these processes in climate models. Demonstration of the ability to conduct such studies by working with prototype laboratory-generated aerosol particles would strengthen any proposal for support of this research from OBER and/or BES. Climate studies and fundamental understanding of processes on a nanoscale are both key strategic elements at BNL. This project brings together capabilities in the pertinent two directorates of BNL, EENS and BES.

APPROACH:

Personnel. Derek Bruzewicz, a post-doc who joined the project in early 2008, conducts laboratory experiments and data analysis; earlier work was initiated by Susan Oatis and Matthew Strasberg (SULI student). Antonio Checco, Ben Ocko (CMPMSD), and Steve Schwartz, Ernie Lewis, and Bob McGraw (ESD) contribute to experimental design and interpretation. Strasberg and Checco developed a feedback system for calibrating and controlling (within ~2%) the relative humidity (RH) in the sample chamber. Bruzewicz has written statistical analysis software to characterize subtle changes in the shape or surface properties of the nanoparticles.

Non-contact AFM was selected as the method of choice for examination of interactions of single particles with water vapor because of the detailed characterization of surface properties and morphology afforded by this method under relevant conditions of atmospheric pressure and relative humidity, with resolution on the scale of a few nanometers. This technique has previously been used by Checco and Ocko to study wetting of prepared surfaces. Aerosol particles of known composition are atomized from solution under ambient conditions and collected on a polished silicon substrate coated with a hydrophobic self-assembled monolayer of octadecyltrichlorosilane (OTS). The size of the deposited aerosol particles can be varied by varying the concentration of the salt solution. Non-contact mode AFM is used because contact between the cantilever tip of the AFM and a particle would deform or destroy the particle. Data from AFM scans provide three-dimensional (3D) profiles of particle morphology at varying relative humidity.

TECHNICAL PROGRESS AND RESULTS:

Initial work reported in December, 2007, measured changes in particle morphology, including deliquescence phase change, as a function of RH for sodium chloride (NaCl) aerosols, a well characterized material selected for our initial AFM studies, deposited on hydrophobic substrates. Recent work has focused on selected flat, rectangular particles, of height approximately 100-150 nm, to simplify the statistical analysis and permit detailed characterization.

Representative 3D profiles of a single NaCl nanoparticle (Figure 1) show an unanticipated distinct change in particle morphology at ~71% RH, well below the deliquescence RH (DRH) of NaCl, 74.5%, with an increase in particle height of ~10%. Previous studies showing wetting of NaCl nanoparticles at higher values of RH, but still below the DRH, used techniques that would not have detected the changes we observe near 71% RH. The apparent pre-wetting of NaCl nanoparticles deposited on a substrate appears (Figure 2) to be reproducible and, in contrast to the deliquescence phase transition, reversible. Despite the uptake of water at the surface the data suggest little solvation and rearrangement below the deliquescence point. These findings have successfully demonstrated that non-contact environmental AFM can characterize quite subtle changes in the particle morphology.

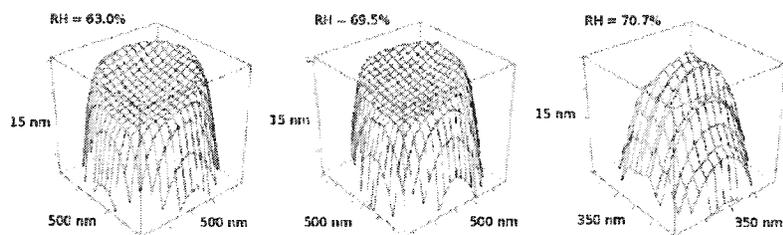


Figure 1: Representative 3D AFM profiles of the top of a 400-nm high NaCl salt nanoparticle at RH 63.0, 69.5, and 70.7% relative humidity.

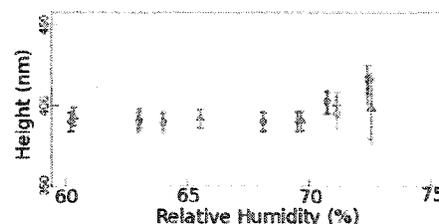


Figure 2: Height of a single NaCl particle as a function of RH in two separate runs.

FUTURE WORK

These studies raise interesting new scientific questions, such as the relationship between the pre-wetting we observe and the shift in DRH for particles of diameter <50 nm reported by Tang and Munkelwitz (*Atmos. Environ.*, 1993). The phenomenon of pre-wetting is interesting physics on its own; other methods have been unable to detect the uptake of so little water. Further experimental and theoretical work is clearly required to characterize this process and its dependence on particle size. In parallel with these experiments, we have started to investigate theoretical explanations of these findings in terms of pertinent free energy quantities. We anticipate further results that will inform atmospheric models and provide a basis for obtaining external support for such studies.

In the coming year this work will be extended to particles with sizes and compositions more directly relevant to ambient atmospheric aerosols. The goal is to catalog pre-wetting and deliquescence as a function of particle size and composition and to determine the influence, if any, of the surface properties of the substrate. A recent upgrade of the instrument has increased output of high-quality data. Future work will include laboratory studies examining dependence on composition and size at RH up to and beyond deliquescence point.

Theoretical interpretation of observations.

Chemical Imaging of Living Cells in Real Time

LDRD Project 07-089

Lisa M. Miller and Roger Phipps

PURPOSE:

The objective of this work is to develop methods for high-resolution, chemical (infrared) imaging of living cells in real time. To date, infrared imaging of biological materials has primarily been performed on dried samples due to the infrared absorbance of water. In addition, most infrared microscopes are equipped with single-element detectors that hamper real-time imaging because the sample needs to be raster-scanned through the infrared beam. Here, we propose to develop a specialized incubator for living cells that is adapted for infrared microscopic imaging in real time. This incubator will be coupled to an infrared microscope with a new focal plane array detector system, where a 128x128 pixel array is used to image large areas quickly. This new technique will become a key element in the ongoing development of biomedical imaging programs at the NSLS that will take advantage of the high brilliance and stability of NSLS-II.

APPROACH:

Synchrotron-based Fourier transform infrared microspectroscopy (FTIRM) is a powerful method for sub-cellular spatial resolution imaging (2-10 μm in the mid-infrared region) of chemical components such as lipids, proteins, nucleic acids and carbohydrates, which are often altered in disease states or in response to external stimuli (e.g. drugs, radiation). One of the major drawbacks of FTIRM is the absorbance of water in the mid-infrared region. The O-H stretching mode of water spans from 3600 – 3100 cm^{-1} and the O-H bending mode overlaps the protein Amide I band ($\sim 1650 \text{ cm}^{-1}$). Due to this potential interference, most FTIRM data on biological cells and tissues published to date have been collected on dried samples.

In this work, we propose a series of developments so the technique can be extended to studying living cells in culture. The motivation behind this new technology is 4-fold: (1) The synchrotron infrared beam is non-ionizing and does not induce any heating effects so samples can be probed for weeks to months. (2) Since FTIR vibrational frequencies are sensitive to isotopic labeling, individual chemical components can be tracked spatially and in real time. (3) This technique can be used simultaneously with other optical-based imaging techniques such as epifluorescence or confocal microscopy and can compliment lower resolution, in vivo techniques such as Positron Emission Tomography (PET) and Magnetic Resonance Imaging (MRI). (4) As part of NSLS-II, infrared beamlines are proposed that will be optimized for infrared imaging. Development of this technology is expected to increase the user base dramatically.

The specific aims of this proposal are to (1) design an incubator for living cells that is compatible with infrared micro-spectroscopic imaging, (2) adapt the infrared imaging microscope with focal plane array detector to a synchrotron infrared beamline at NSLS and (3) apply the newly developed technology to study bone mineral production and the effects of a current, isotopically-labeled osteoporosis drug on this process.

TECHNICAL PROGRESS AND RESULTS:

During FY07, Dr. Bodendiek found that ZnSe was an acceptable ATR substrate for the growth and adherence of cells in culture. Thus, in FY 2008, we proceeded to grow fibroblasts on a ZnSe hemisphere. A specialized Teflon holder was designed so that the hemisphere would stand upright and cells would not grow on the curved surface. After the cells were grown in the hemisphere, the hemisphere was removed from the cell culture medium, washed with PBS, and the cells were allowed to dry. The hemisphere was flipped, mounted at beamline U10B, and an FTIR image was collected with an

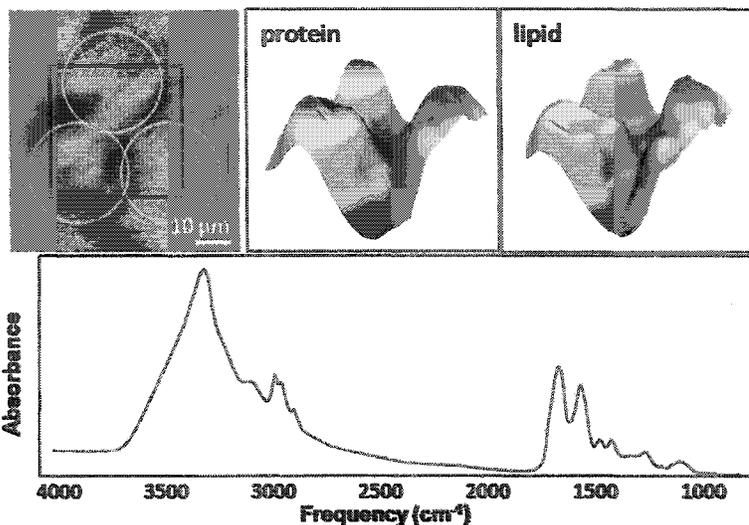


Figure 1. (Top left) Light micrograph of dried fibroblasts on ZnSe hemisphere. White circles indicate individual cells. Red box indicates area mapped with the FTIR microscope. (Top right) Protein and lipid distributions from the FTIR image. (Bottom) Sample FTIR spectrum from the cells on the hemisphere.

aperture (beam) size of 10 μm . The results can be seen in **Figure 1**. The light micrograph is blurry because the camera was mounted above the hemisphere so the photo was taken through the ZnSe. One improvement to make on the final design will be to mount the camera for front-side illumination for a better optical image. A sample spectrum and FTIR images of the protein and lipid distributions can also be seen in **Figure 1**. The signal-to-noise of the spectrum is excellent, even below 1000 cm^{-1} . The protein image illustrates that the protein distribution is relatively uniform throughout the cell, but highest in the center (i.e. the nucleus). Conversely, the lipid distribution is highest near the edges of the cells, which are consistent with the cell membrane. Ongoing efforts in FY 2009 involve examination of wet cells on the hemisphere and the development of algorithms for water correction in the spectra.

Also in FY08, we were able to couple the focal plane array FTIR detector to the synchrotron. For the initial tests, a single illumination optic was used. With this configuration, approximately $\frac{1}{4}$ of the array was illuminated, which saturated the detector. Ongoing efforts in FY 2009 involve the design of a multiple-mirror or curve-mirror system, in order to collect a larger opening angle of light from the synchrotron and to illuminate the detector uniformly. In addition, a 74X objective will be used to illuminate a 32 μm area of the sample with 0.5 μm pixel resolution. Point spread function deconvolution algorithms are being designed for the Schwarzschild FTIR objective in order to further improve the spatial resolution of the images. By combining synchrotron light with 10X oversampling and a sample substrate with a high index of refraction, we hope to image living cells at a resolution of $< 1 \mu\text{m}$.

Coherent Bragg Rod Analysis of High-T_c Superconducting Epitaxial Films

LDRD Project 07-090

Ron Pindak

PURPOSE:

Recent years witnessed an exciting discovery of interface superconductivity in complex oxides. In particular, bilayers films consisting of a non-superconducting metal La_{1.55}Sr_{0.45}CuO₄ (LSCO) and an insulator La₂CuO₄ (LCO) on La₂AlO₄ substrates showed superconductivity with the critical temperature T_c ≈ 30 K, occurring in an interfacial layer about one unit cell (1UC) thick [1]. The origin of the interfacial superconductivity and T_c enhancement is a matter of intense current debate; the *scientific objective* of this LDRD is, through a better understanding of structural changes, to gain insights on how we might unlock a way to enhance T_c even further.

The four *technical objectives* of this LDRD project required to achieve its *scientific objective* include. (1) The measurement of complete sets of symmetry inequivalent Bragg rods for different complex oxide thin films. The first example is the bilayer samples studied in Ref. [1], which are composed of m UCs of metallic LSCO and n UCs of insulating LCO, which we refer to as (m,n) bilayers. The measurements are followed by analysis using the COBRA phase retrieval method to provide 3D electron density (ED) maps with unprecedented convergence speed and precision. (2) The measurement and analysis of Bragg rods at different energies across the edge of a dopant atom to determine the dopant concentration dependence normal to the substrate. In the (m,n) bilayers, Sr substitutes for La in LCO. This is an important measurement since a UC with the appropriate Sr concentration might become superconducting. (3) The extension of the COBRA method to determine model-independent, in-plane averaged 1D ED maps from X-ray specular diffraction measurements. This can be done at the NSLS. Phase retrieval in 1D is notoriously difficult to achieve. (4) Develop the instrumentation at the NSLS to do the complete set of Bragg rod measurements required for COBRA analysis using the Wiggler Beamline X21.

APPROACH:

The combination of high brightness insertion device X-ray sources, efficient and precise surface X-ray diffraction measurements using new pixel array detectors, and new phase retrieval methods have resulted in model-independent structural determinations of a growing number of physical systems. High-precision Bragg rod measurements will be carried out using the high-brightness Advanced Photon Source (APS) and the Swiss Light Source (SLS) synchrotron facilities. The COBRA phase retrieval method, developed by two investigators on this LDRD (Pindak and Yacoby) together with R. Clark, will be applied to the diffraction data and the method refined as necessary to meet the project's technical objectives. A post-doctoral research associate, Hua Zhou, joined the diffraction measurement and analysis team in November 2007.

Other investigators on the LDRD, I. Bozovic, V. Butko, and G. Logvenov (CMPMSD) will prepare complex oxide epitaxial systems of various types that exhibit high-T_c superconductivity using their ALL-MBE growth facility and characterize the thermal and transport properties exhibited by these films.

TECHNICAL PROGRESS AND RESULTS:

Technical Objective 1 -- Complete sets of Bragg rod measurements were taken using beamline ID-33 at the APS on two different LSCO/LCO bilayers: (3,3) and (3,2). To improve accuracy of

the electron density (ED) maps, the data was analyzed first by the COBRA phase retrieval method, and then the results were further refined by the Difference-Mapping method resulting in convergence to ED maps with a reliability factor of 0.02 (comparable or better than other published Bragg rod analyses); but, with convergence in 27 iterations compared to over 2000 iterations required by other approaches. The ED maps enabled us to accurately determine the positions of all the atoms including oxygen in the LSCO/LCO UCs with sub-Ångstrom resolution. Combining transport and X-ray measurements, we arrived at the following conclusions [2]: (1) Sharp superconducting transitions were observed at $T_c = 34$ K in the (3,2) and $T_c = 36$ K in the (3,3) bilayer, significantly higher than the values reported for (n,m) bilayers in Ref. [1], which is remarkable given that these films are only 5-6 UC thick. (2) The measured lattice constants of the bilayer film were the same for all UCs and had a value of $c_0 = 13.304$ Å, which was larger by 0.131 Å than that of the bulk LCO. This was expected from the strain and elastic properties. (3) However, quite unexpectedly, we observed large variations in the Cu-apical O and La-apical O distances. In the metal layer closest to the substrate the Cu-apical O distance was 0.11 Å smaller than the bulk LSCO (LCO) Cu-apical O distance and steadily increased to being 0.34 Å larger at the surface - a remarkable change of 0.45 Å. Variations in the apical oxygen position are known to strongly affect T_c . We conclude that in cuprates the crystal structure can be modified in near-surface layers, and in such a way that superconductive properties are dramatically altered. In order to further elucidate whether the change in the Cu-apical O distance is being driven by the surface or by the metal/insulator interface, we've planned a series of experiments on single phase systems as well as inverse LCO/LSCO systems in which the number of LSCO layers will be systematically varied. Beam time has been allocated at the SLS for these measurements.

Technical Objective 2 -- we attempted to measure a complete set of Bragg rods at energies above and below the Sr-edge; however, COBRA analysis did not succeed at yielding a robust Sr concentration profile. Two difficulties were identified that will be corrected in subsequent runs: (1) although data was taken over a wide Q_z -range from 1.0 to 10.5 reciprocal lattice units, the missing low- Q_z data enabled different slowly varying concentration profiles to give equally good fits and (2) there were variations in incident flux that were difficult to correct between data sets. To address these difficulties, we developed a new Differential COBRA method that involves measurements for each Bragg rod point at 3 energies: the energy of minimum diffraction cross section for the constituent atom, slightly above and below. We applied for beam time to test.

Technical Objective 3 -- using Specular Reflectivity data from the (3, 3) and (3, 2) LSCO/LCO bilayer samples, we attempted to do a 1D model-independent COBRA analysis. The results were not robust indicating that an additional constraint is required. As done for objective 2, a Differential Reflectivity method will be used. NSLS beamline X6B is suitable for this measurement and beam time has been awarded.

Technical Objective 4 -- neither the NSLS FY08 nor initial FY09 budgets had adequate funds to procure the Psi 2+4 Circle Diffractometer required to implement Bragg rod measurements on the NSLS X21 wiggler beamline. We will not be able to complete this last objective, which involved an instrument intended for transfer to NSLS-II. For this reason, we expanded our collaboration to include Phil Willmott of the SLS so that we could utilize the Surface Diffractometer at this synchrotron facility as well as the one at the APS.

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- [2] "Anomalous Expansion of the Cu-Apical O Distance in Superconducting $\text{La}_2\text{CuO}_4 - \text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4$ Bilayers", H. Zhou, Y. Yacoby, R. Pindak, V. Butko, G. Logvenov, and I. Bozovic, manuscript in preparation.

Development of Planar Device Technology for Hyperpure Germanium X-ray Detectors

LDRD Project 07-091

Peter Siddons, Abdul K. Rumaiz, Gabriella Carini and Pavel Rehak

PURPOSE:

The higher mobility of carriers combined with a low effective mass in Germanium (Ge) as compared to Silicon (Si) has generated a lot of interest in Ge based devices. This is particularly so in X-ray radiation detectors where Si based detectors become transparent at higher X-ray energy. Although higher energy X-ray beams are regarded as very fascinating and useful implements offered by Synchrotron facility (especially with the new NSLS II) to materials/biological sciences, the existing detector technology does not let us yet to fully utilize this energy region. Our work is to address this issue and to develop a process for making robust Ge based X-ray detectors.

APPROACH:

Ge has been regarded as a replacement for Si in convention X-ray detectors due to the higher atomic mass. It has also been currently studied as a replacement for Si as the channel material for high speed CMOS technology. Ge has higher electron and hole mobility and a lower effective mass [1]. The key challenge in realizing a Ge based detectors is having a stable oxide since the native oxide is highly unstable. During the last few decades several dielectric material such as SiO₂, Al₂O₃, Ge oxynitride have been attempted as potential oxide barrier layer for Ge, although none of them could offer a reasonable effective oxide thickness [2,3,4]. In light of the recent success of the high- κ dielectric deposition in Si [5], we are investigating the possibility of using high- κ dielectric for Ge based detector.

The other problem associated with Ge processing is heat. It has been known that any high temperature processing over 400 °C diffuses the hydrogen (which is used to passivate the Cu impurity) out of the system. This is an added concern which needs to be addressed in all our semiconductor processing. We have chosen Zirconium oxide (ZrO₂) as the high- κ dielectric for our study because of the ease of synthesis and a lower reported interfacial defect density [6]. We have deposited ZrO₂ films by metal deposition followed by a UV ozone oxidation. This technique has been successful in creating high quality ZrO₂ without the need for high temperatures.

TECHNICAL PROGRESS AND RESULTS:

We have hired a postdoc (Abdul K Rumaiz) who started working from Nov. '07. After some literature survey a suitable implants and oxide was identified. A dual sputter gun metal deposition/oxidation system was constructed and is now fully operational. Hydrogen evolution studies confirmed the problem of hydrogen diffusion, which has put a constrain in our wafer processing.

We have synthesized ZrO₂ by depositing metal Zr and subsequent UV ozone oxidation on Ge/GeO substrates. Since this technique is less energetic (than plasma oxidation) we did some high energy X-ray photoelectron spectroscopy (XPS) at beamline X24A to verify the oxidation state of Zr. Figure 1 one shows high resolution spectra of Zr 3p core level peak. The peaks at 332.8 and 346.6 are the characteristics 3p_{3/2} and 3p_{1/2} spin doublet from Zr⁴⁺ [7]. We have used

this the 3p core peak instead of the 3d peak because of a overlap of Ge 3s peak with the Zr 3d peak. The inset in figure 1 shows the O 1s spectra taken at normal incidence and at glancing angle. The peaks can clearly be deconvoluted into two components. The higher binding energy (HBE) component is from oxygen from ZrO_2 while the weak lower binding energy (LBE) is from oxygen from the surface oxide of Ge. As expected

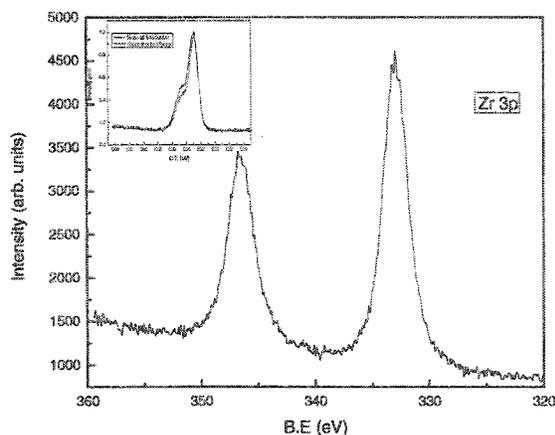
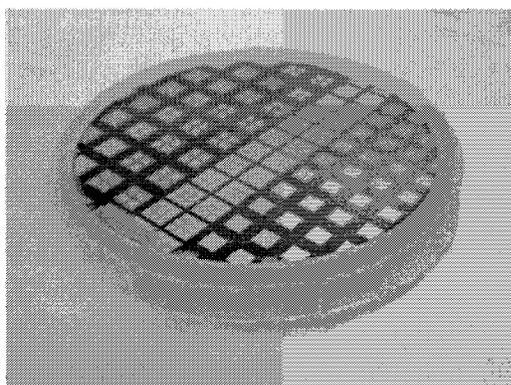


Figure 1: XPS high resolution spectra of Zr 3p region

the peak intensity of LBE goes down at glancing angle since the penetration depth of X-ray is less. This also confirms the presence of GeO layer. Further work in understanding the Fermi level pinning of the barrier oxide and its correlation on the intermediate oxide layer is currently underway in collaboration with Dr Joseph Woick at NIST.

A simple diode structure with Ge/GeO/ ZrO_2 (25 nm)/Al (200 nm) was created using stand lithographic technique. Figure 2 shows the diode structure on a 3 inch Ge wafer. The Capacitance-voltage measurement done in these structure is shown in figure 3. The value of the capacitance obtained is fairly close to the calculated value. The CV measurement shows an obvious hysteresis which is indicative of interfacial defects. The inset of figure 3 shows the leakage current measured. The value of leakage current is close to some reported values measured in similar system. The interfacial defects can be reasonable controlled by annealing and also by creating some intermediate layers (like oxynitride and sulphide) between Ge and ZrO_2 . These are some works which are currently being addressed.

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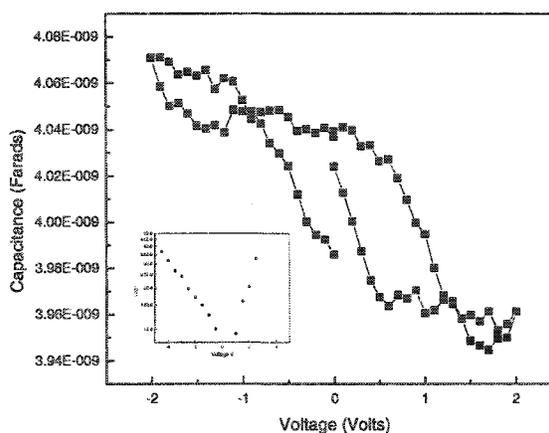


Figure 3: CV measurement at 100 kHz

Milestones:

6 month: Low defect high- κ dielectric fabrication process finalized. Simple monolithic diode arrays fabricated.

1 year: Ge drift detector structure fabricated and tested.

Study of Epigenetic Mechanisms in a Model of Depression

LDRD Project 07-096

Fritz A. Henn

PURPOSE:

The project was initially conceived as an investigation into the circuits mediating depression and the gene changes caused by early life stress which might modify these circuits. The hope was to define the alterations caused by stress which would lead to the disease of depression. Defining the genes responsible and the circuits involved, would provide information for the development of new treatment approaches. However, in view of technical challenges this project has bifurcated. We continued the depression project with a narrow focus on drug development and chose to initiate a new project aimed at looking at the effect of changes in temperature and CO₂ content on changes in gene expression in plants, i.e., the epigenetics of climate change. In view of the success we have had in defining the circuits involved in depression, we have focused on the control of these circuits using electrophysiology and microdialysis with the goal of defining novel potential sites for antidepressant drug development. The plant project became the primary effort of Dr. Liu and has resulted in the establishment of a new lab for this purpose and the hiring of a post doctoral fellow in this area through the LDRD. The goal here is to build a bridge between atmospheric science and biology related to biofuels production. This has been presented top BER last week as a potential growth area which they are considering.

APPROACH:

Project 1: The use of inbred strains of rats developed over many years, one of which was susceptible to learned helplessness, an analog of human depression and one which was resistant to stress and learned helplessness allowed us to define a circuit which was overactive in the helpless condition. This circuit involved a structure, the lateral habenula, which appeared to act as a control point defining the change in affect and behavior. This structure appears to be overactive in helplessness and by analogy in depression. We have used PET imaging, structural MR and microdialysis and behavioral analysis at Brookhaven and electrophysiology done in collaboration with the Malinow Lab at Cold Spring Harbor and then following a move at UCSD to define the defect at the habenular synapse. A collaborative effort involved the NIMH imaging group to verify the overactivity in human depressed patients.

The use of these strains allows us to ask if the vulnerability has to do with the genes defining the different strains. Both strains have been exposed to stress early in life and gene arrays for differential expression have been constructed in co-operation with nimblegene and we will begin looking at the differences as a result of the strain background.

Project 2: Dr. Liu set up a lab and growth chambers to expose aridopsis to varying CO₂ concentrations and temperatures, she hired a post doctoral fellow and has developed gene arrays working with nimblegene to begin a study of gene expression changes as a function of these 2 variables. The approach is straight forward to initially look at the methylation patterns as a function of temperature and CO₂ concentration.

TECHNICAL PROGRESS AND RESULTS:

Project 1: The circuit has been defined using animal imaging and human imaging, overactivity has been demonstrated in the animals with considerable precision, and the synapses are being

defined using selected inhibitors. In humans, overactivity was demonstrated and neurosurgical intervention using deep brain stimulation to inhibit the habenula was carried out by collaborators in Heidelberg Germany with good results. We determined, using binding studies and microdialysis, a likely cause of pathology within this circuit was excessive glutamatergic activity due to decreased astrocytic transport of glutamate from the synaptic cleft. We were able to reverse helplessness, using compounds known to increase glutamate transport, suggesting a new target for antidepressant drug development. A patent application is being filed this month for the use of K_{ATPase} channel openers as antidepressants since they increase glutamate uptake by astrocytes. The coming year should see NIH funding to continue this project and the development of new antidepressant drugs, ideally with corporate funding. Two publications are in press and a major grant has been submitted.

- Milestones:
1. Patent filing - this calendar year
 2. Papers on Mechanism - 2 high profile within 6 months
 3. Deal with a major pharmaceutical firm within this fiscal year

Project 2: The foundation has been laid for obtaining information on gene changes caused by climate change. The data will be gathered next year and presented to BER as the foundation for a larger epigenetic study of the effects of climate change. An initial step is the determination of the methylation levels of the aridopsis gene which is being done in collaboration with a group at Johns Hopkins and is currently underway. A method using HPLC to look at methylation is being developed and should be applied within 3 months.

- Milestones:
1. First data on role of T and CO_2 in altering gene expression within 6 months.
 2. Presentation to BER in the Spring – Summer
 3. SFA for the next fiscal year written within this year.

Polarized Electron SRF Gun

LDRD Project 07-097

Ilan Ben-Zvi and Jörg Kewisch

PURPOSE:

The purpose of the project is to carry out research on the feasibility of using a superconducting, laser-photocathode RF electron gun (SRF photoinjector) for the production of polarized electrons. We expect to show that a cesiated gallium arsenide photocathode (which is necessary for the production of polarized beams) maintains its quantum efficiency in an RF gun and that the migration of cesium from the cathode to the SRF cavity is so small that the properties of the gun will not be affected. This is a most desirable result since SRF guns outperform DC guns for high brightness beams. The motivation of this research is twofold: First, demonstrate that a SRF photoinjector can be used at the International Linear Collider (ILC) to eliminate the need for an electron damping ring. Second, such a gun would be at the heart of the linac for eRHIC, thus having a large impact on the future of the QCD laboratory strategic initiative at BNL.

APPROACH:

State-of-the-art polarized electron guns rely on the use of direct band gap III/V semiconductor NEA cathodes. When illuminated with circularly polarized laser light the cathode emits polarized electrons. Cathodes made of strained GaAs have been especially successful. The laser excites electrons from the valence band into the conduction band. To achieve reasonable emission efficiency the work function of the material has to be lowered. This can be accomplished by adding a monolayer Cesium and oxide to the surface[i]. This surface layer is subject to rapid aging, which leads to a decrease of quantum efficiency of the cathode.

In DC polarized guns, we recognize two main contributions to the cathode aging process: Oxidation through reaction with the background residual gas in the vacuum system and ion impact on the cathode surface will both lead to degradation of the quantum efficiency. Both effects are proportional to the vacuum pressure in the gun. While DC guns typically have a vacuum pressure of 10^{-11} torr, a normal conducting RF gun reaches only 10^{-9} torr due to outgassing caused by the RF field. Under such conditions the cathode life time can be as short as 10 seconds [iii]. In a superconducting RF gun the cryo-pumping of the cavity walls improves the vacuum and the pressure can match that of a DC gun. While in a DC gun all ions are accelerated towards the cathode, only ions generated at the correct RF phase will reach the cathode and the maximum kinetic energy is limited due to their high masses. With identical vacuum conditions the ion back-bombardment in a SRF gun can be an order of magnitude lower [ii]. In an RF gun, electron back bombardment is an additional cause of concern. The source of these electrons is field emission in the gun. However, the same extensive cleaning procedures that are used to improve the quality factor (Q) of the SRF gun cavity have been proven to reduce field emissions significantly.

The experiment consists of three major parts: a cryostat containing a 1.3 GHz SRF electron gun with a beam transport system, vacuum system and diagnostics; a cathode preparation chamber for the development of a strained gallium arsenide, cesiated photo-cathode under ultra-high vacuum (10^{-11} torr or better) and a transporter system allowing to move the cathode between the two systems while maintaining an ultra high vacuum. We use parts that became available from other projects to the largest extent possible.

The goal of the experiment is the measurement of the quantum efficiency lifetime of the cathode and the SRF performance of the gun over sufficiently long time to demonstrate the compatibility of the cathode with SRF performance and the compatibility of operation of the photocathode in high RF field in the gun.

TECHNICAL PROGRESS AND RESULTS:

In 2008 all critical parts of the system were produced or purchased and delivered: the 90 degree dipole and vacuum chamber with ports were build in-house, the permanent focusing magnet design was replaced by a high-temperature superconductive solenoid built by the magnet division. This eliminates the need of field compensation since the magnet is turned off during cool down. The transporter mechanism (actuator, valves, clamp, cathode plugs) as well as NEG and ion vacuum pumps were purchased.. The cathode preparation chamber has been assembled and pumped down. The vacuum level is currently 10^{-10} torr, and is improved by baking. The cesiation system was purchased and tested. The produced cesium layer has excellent uniformity. A stalk heater system for the regeneration of GaAs cathodes at up to 620° C was calibrated.

The gun has been cooled to 4.2° K and was tested with a network analyzer, verifying the quality measured at Jefferson Lab. Using only the cryogenic pumping of the gun the vacuum pressure was better than 10^{-11} torr.

The initially planned parasitic use of the ERL cave is not possible because of the limited height of the cave. Instead, a new radiation protection enclosure will be built from existing concrete shielding blocks. The new enclosure has been designed and blessed by the safety exerts.

Ion back-bombardment and electron back-bombardment has been studied analytically and with computer simulations. It has been shown [iv] that only a fraction of the created ions can reach the cathode and will impact with energies up to 1 keV instead (compared to hundreds of keV in DC guns.) Electrons can impact the cathode with energies up to 350keV, but will dislocate GaAs molecules only if the impact energy is above 300 keV. However, simulations indicate that in [iii] the impacting electron can create a large number of secondary electrons capable of returning to the cathode and therefore create an electron shower[v]. This is not expected in our experiment because of the lower frequency and different geometry of our gun.

Time line for 2009: The preparation chamber will be completely assembled and pumped down to a vacuum pressure of 10-11 torr by January 15th. At that time cathode preparation and transport can be tested. The RF gun assembly will be ready by February 15th, allowing low power RF testing without beam. The concrete enclosure and its interlock system is expected to be completed by March 1st, the experimental results are expected in April.

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New Approach to H Production, Stages and Use

LDRD Project 07-098

Weiqliang Han

PURPOSE:

Hydrogen has great potential as an environmentally clean energy fuel and as a way to reduce reliance on imported energy sources. This requires safe and efficient hydrogen production, transportation, conversion and storage. In this project, we work on designing, synthesizing and characterizing new nanomaterials that have the possibility of meeting the criteria for high-efficiency hydrogen producing based on water-gas shifting (WGS) reaction and hydrogen storage based on boron nitride nanostructures.

APPROACH:

To study high-activity and high-selectivity heterogeneous catalysts of oxide and metals, we worked on designing and synthesis of new nanostructures of oxides and noble metals, including Cu-doped CeO₂, Magnéli phases Ti_nO_{2n-1} nanowires, and Pt, Pd, PtAu, Pd Au, Rh ultrathin nanowires. We test these heterogeneous catalysts for WGS reaction.

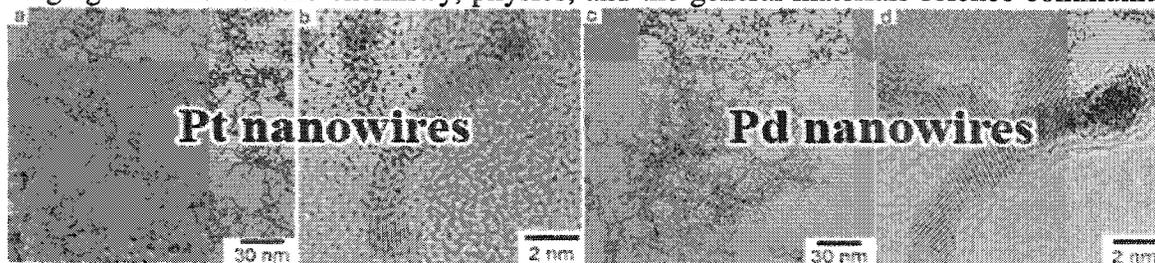
Experimentally, it is extremely difficult to identify the exact active sites in the metal/oxide catalysts for WGS reaction. We have started DFT calculations to understand the active sites and reaction mechanism for the WGS on metal/oxide (Au/CeO₂, TiO₂), metal carbide (Mo₂C) and metal phosphide (Ni₂P), which have recently been reported to be very efficient catalysts for the WGS reaction.

To study doped BN nanotubes, mono- and few-layers BN sheets for the possible applications of hydrogen storage and solid state ultraviolet light source.

TECHNICAL PROGRESS AND RESULTS:

1. A new method is developed to prepare one-dimensional (1D) Cu-doped CeO₂, whose diameters are around 10 nm. Without adding extra noble-metals, one-dimensional (1D) Cu-doped CeO₂ shows catalytic activity for WGS reaction starting at quite low-temperature 150 °C.
2. A new synthesis method is developed to synthesize Magnéli phases Ti_nO_{2n-1} nanowires, such as triclinic Ti₈O₁₅ nanowires and Ti₄O₇ quasi one-dimensional fibers. In contrast to wide-bandgap semiconducting tetragonal-TiO₂, both Ti₈O₁₅ and Ti₄O₇ exhibit high electrical conducting behavior at room temperature. The electrical conductivities of Ti₈O₁₅ and Ti₄O₇ are, respectively, 0.24 S/cm, and 10.4 S/cm at 300 K, and 2.4×10⁻⁵ S/cm, and 4×10⁻³ S/cm at 77K. In both materials, the light absorption band covers the full visible-light spectrum region and extends into the near-infrared region. These materials are expected to be used in gas sensors, battery electrodes, and photoelectrolysis.
3. Using a phase transfer method, we succeeded in first synthesizing ultrathin palladium and platinum nanowires (< 2.5 nm in width) and the observation of novel magnetic properties in these nanowires. Our results demonstrate the unique features of one dimensionality and

localization of electronic states in conventional nonmagnetic metals, and will have a wide ranging influence on the chemistry, physics, and the general materials-science communities.



4. We developed a new synthesis route to prepare Au/Pd alloy nanostructure through the galvanic replacement reaction between Pd ultrathin nanowires and AuCl_3 in toluene. We monitored both morphological and structural changes during the reaction for up to 10 hours. Continuous changing of chemical composition and crystalline structure from Pd nanowires to $\text{Pd}_{68}\text{Au}_{32}$ and $\text{Pd}_{45}\text{Au}_{55}$ alloys and Au nanoparticles was observed. These nano-noble metals are expected to have great potential as catalysts for hydrogen production.
5. We developed a new synthesis route to make Pt/Au hybrid nanowires. More interestingly, by using X-ray absorption (XAS) spectroscopy technique, charge transfer upon hybrids formation was observed, that d-charge depletion occurred at the Pt site, accompanied by d-charge gain at the Au site. The reported methodology to synthesize Pt/Au hybrid nanowires and study of electronic structure of Pt/Au hybrids will be of great importance in catalysis and materials science.
6. Incorporating with extensive experimental efforts, we performed DFT calculations to investigate the WGS reaction on Au(100), Au_{29} nanoparticles, Au nanoparticles supported on $\text{TiO}_2(110)$ and TiO_2 nanoparticle supported on Au(111). According to our calculations, the bottleneck of the WGS reaction on Au is overcome by combining Au with TiO_2 . CO adsorbs at the Au sites and water can be easily dissociated at the oxide. The rests of the reactions are able to proceed at a reasonable speed at the Au- TiO_2 interface. The rate limiting step (rls) for the WGS reaction on Au/ $\text{TiO}_2(110)$ and $\text{TiO}_2/\text{Au}(111)$ is the formation of carboxyl (HOCO^*). However, in both cases, the corresponding barriers for the rls are lower than these for water dissociation on Au_{29} and Au(100), and therefore a better WGS activity is expected. This agrees well with the experimental observations. The corporation between oxide and metal was also observed for the WGS reaction on Mo_2C and Ni_2P using DFT, where Mo oxycarbide and Ni oxyphosphide was identified as the active phase under the WGS conditions, respectively. Overall, our study show that the good WGS performances rely heavily on the corporation between oxygen and metal centers with moderate activity.
7. We carried an isotope study on the bandgap and radiative transition spectra of BN nanotubes. The rich CL spectra between 3.0 eV – 4.2 eV reflect a phonon-electron coupling mechanism. We suggest that those radiative transitions in BNNTs could be generated by a replacement of some nitrogen atoms with oxygen atoms. This study is expected very helpful for developing prospective nano-devices, such as ultraviolet laser and ultraviolet LED. The demonstration of oxygen doping indicates that the possibility of doping of other elements, which may lead an efficient route for hydrogen storage.

8. We developed a chemical-solution-derived method to prepare mono- and few-layer hexagonal sheets and study their microstructure and electrical properties.
9. We have studied the storage and phase transformation of hydrogen and methane inside BN nanotubes through a high-pressure technology.

High End Scientific Computing

LDRD Project 07-101

James Davenport and Sam Aronson

PURPOSE:

The purpose of this LDRD is to establish at BNL, a laboratory competence in the efficient and effective utilization of large-scale, high-end computers in support of our multi-program research environment. The goal is to increase the number of applications which can take advantage of the new machines which are being deployed throughout the DOE complex.

We will accomplish this task by bringing together scientific expertise in laboratory mission areas with experts in computational science, applied mathematics, and computer operations.

APPROACH:

The current direction in high end computing is to build massively parallel machines with tens to hundreds of thousands of processors connected through complex communication networks. IBM's Blue Gene architecture is one example of such a machine, which currently is among the world's fastest. In collaboration with Stony Brook University, BNL acquired a 100 teraflops Blue Gene/L in 2007 and a 28 teraflops Blue Gene/P in 2008. Called New York Blue, these machines contain 36,864 and 8,192 processors respectively and are orders of magnitude faster than typical departmental cluster computers. This unique resource enables investigations that are of a scale and complexity previously unavailable to BNL scientists. To further the goals, a CRADA has been established with Stony Brook University and the Research Foundation of SUNY.

Unfortunately, most codes and algorithms are not designed to take advantage of the immense power these machines offer. Typically, dividing a large problem among many processors does not lead to a comparable speed up in the calculation because of an imbalance between computation and communication. Therefore most codes need to be rewritten to be effective in this environment. This process requires a team approach with expertise in the scientific, mathematical and computational aspects brought to bear.

This project therefore involves a large number of collaborators in nuclear and elementary particle physics, nanoscience, computational biology, applied mathematics, fluid dynamics, and climate modeling. Numerous such teams have formed and are now producing results.

TECHNICAL PROGRESS AND RESULTS:

Blue Gene/L has been in full operation since November 2007 and Blue Gene/P since January 2008. There are currently 250 authorized users with 170 accounts. Utilization has consistently been approximately 95% of the cycles each month. This year the batch system, LoadLevelor, has been coupled to the individual account allocation data base. An additional 160 terabytes of disk storage and 460 terabytes of tape archival and back up storage have been added. Scaling studies (showing how various codes speed up with increasing number of processors) have been conducted in several fields. A climate model has run on the full Blue Gene/L machine. Codes have been ported and run in a wide range of disciplines including computational biology, quantum chromodynamics, nanoscience, climate modeling, astrophysics, fusion, accelerator design, and fluid dynamics. More than 30 publications are in press or submitted based on work

done on the machines. Nine posters and a movie were presented at the Annual SuperComputer conference in Austin Texas.

In summary, operations are going well with results in a wide range of scientific disciplines, by a large number of users and with numerous publications.

Milestones for 2009:

- Obtain Non-DOE funding to support this effort
- Continue to improve the scheduler to favor massively parallel runs
- Complete porting of codes for Materials and NanoScience
- Add Projects in Accelerator Design

How Does Color Flow in a Large Nucleus: Exploring the *Chromo*-Dynamics of QCD through Diffractive and Jet Measurements at eRHIC

LDRD Project 08-001

Raju Venugopalan

PURPOSE:

An important aspect of Quantum Chromodynamics (QCD) studies with eRHIC is to understand how the fundamental quark and gluon fields manifest themselves in nuclei. A key property of quarks and gluons is their “color” charge and their *chromo*-dynamics is what distinguishes the strong interactions from other fundamental forces in nature. The flow of color in nuclei differs greatly from process to process. The LDRD project is focused on understanding the *chromo*-dynamics of two processes in deeply inelastic scattering off nuclei at high energies: a) diffraction and b) jet production. The purpose of studies with the former is to explore whether diffraction off light and heavy nuclei at an electron ion collider can provide an unambiguous signature of strong color field dynamics in QCD—in particular a putative novel saturated form of matter called the “Color Glass Condensate” (CGC). Jet studies, while also providing a novel channel to measure the nuclear gluon distribution, may provide a powerful diagnostic tool of the interaction of colored particles with an extended colored medium. As eRHIC, if realized, will be the world’s first electron nucleus collider, our objective is to develop these exploratory studies to eventually incorporate them in Monte-Carlo generators for nuclear deep inelastic scattering (DIS). These will be valuable in optimizing detector and accelerator design studies to extract the novel physics promise of eRHIC.

APPROACH:

In attacking the problem of nuclear diffraction, it was decided that dipole models that easily incorporate the saturated CGC physics offered much promise. Such dipole models had previously been applied to study the DIS data from electron proton scattering experiments at the HERA collider in Germany. However a consistent application to *all* the relevant HERA data (especially diffractive data) was lacking. The PI and colleagues decided to first obtain a consistent treatment of this data in the dipole framework and then subsequently develop techniques to apply this approach to nuclei. An important constraint was to make sure that the results were consistent with the available nuclear data from earlier experiments. With regard to jet studies, the goal was to employ novel state of the art jet finding techniques developed by co-investigators Gregory Soyez and Gavin Salam to reliably determine the gluon distribution in different kinematic ranges. (The other investigator is Werner Vogelsang who offers general expertise on all issues related to perturbative QCD.) The strategy adopted (in a staged approach) was to first apply the jet finder development work to RHIC and LHC heavy ion collisions. This is because they provide much more stringent tests of jet finder techniques than nuclear DIS. These techniques would then be extended to nuclear DIS to extract complementary information on nuclear gluon distributions. The final step is use of jet techniques as a diagnostic tool for new physics.

TECHNICAL PROGRESS AND RESULTS:

The dipole approach alluded to above was successfully applied to give a consistent description of HERA data. Important to a consistent description are the treatment of the heavy quark contribution [1] and the impact parameter dependence of the dipole cross-section [2]—both of these issues were addressed by Gregory Soyez, who was hired as a research associate on the LDRD. As a first test of its extension to nuclei, it was shown that “inclusive” nuclear data from previous nuclear DIS (fixed target) experiments could be reproduced with no additional parameters [3]. This approach could then be extended to diffractive nuclear scattering. A first

detailed study was performed and published in [4]. (See also [5] for a briefer presentation.). In performing these studies, we had valuable technical advice from Henry Kowalski from DESY, Alberto Accardi and Vadim Guzey from JLAB, who visited us under the aegis of the LDRD.

A novel feature of this study was to separate coherent nuclear diffraction (the nucleus remains intact) from incoherent nuclear diffraction (the nucleus breaks up into nucleons). This is potentially very important for eRHIC because incoherent diffraction can be measured while coherent diffraction on heavy nuclei can only be inferred (except perhaps for light nuclei). Currently, there is considerable independent work by Matt Lamont and Thomas Ullrich of STAR to develop a Monte Carlo (MC) event generator for diffraction modeled on the HERA MC generator RAPGAP. We hope to embed our studies of incoherent diffraction within this MC in order to develop a clearer picture of the nuclear fragments in incoherent diffraction. About 25% of all events in nuclear DIS are diffractive and 30% of these are incoherent—these processes are therefore a significant part of the total cross-section and therefore a significant potential diagnostic tool of color (less) diffractive dynamics at eRHIC. Discussions with Lamont and Ullrich on implementing ideas along with Cyrille Marquet (Columbia U.) are promising and are a challenging milestone for this project.

In jet studies, there has been considerable progress under the LDRD (see Refs. [6,7,8,9]) in development of jet finder algorithms by Salam and Soyez (in collaboration with Matteo Cacciari of Univ. of Paris). The SIS cone and anti- k_t algorithms developed by them are free of known pathologies of earlier jet finding algorithms. These jet studies are now being developed for eRHIC and first results will be presented at the electron ion collider collaboration meeting in Berkeley in December. A milestone for this aspect of the LDRD is to prepare a detailed note of the prospects from these jet studies (for different energies and kinematic cuts) for extracting nuclear gluon distributions at eRHIC as well as the use of jets as a tool to extract other properties of the colored medium.

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- 2) “Travelling waves and impact-parameter correlations”, *S. Munier, G. Salam and G. Soyez*, [arXiv:0807.2870](#).
- 3) “Nucléar enhancement of universal dynamics of high parton densities”, *H. Kowalski, T. Lappi and R. Venugopalan*, *Phys. Rev. Lett.* **100**:022303 (2008).
- 4) “Nuclear enhancement and suppression of diffraction structure functions”, *H. Kowalski, T. Lappi, C. Marquet and R. Venugopalan*, *Phys. Rev. C* **78**, 045201 (2008).
- 5) “Nuclear diffractive structure functions at high energies”, [arXiv:0805.4809](#), *C. Marquet et al.*, presented at the 43rd Rencontres de Moriond on QCD, March 2008.
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Strongly Correlated Systems: From Graphene to Quark-Gluon Plasma

LDRD Project 08-002

D. E. Kharzeev and A. M. Tsvetik

Purpose:

Our goal is to develop schemes of spintronic devices for spin control and manipulation of carriers in magnetized graphene. The basic element of any such device contains conducting regions with different magnetization. The lateral boundary between such regions comprises the *domain wall*. The technical objective of our project is to study the spin-dependent transport through the domain wall.

Approach:

The field of spintronics deals with the development of devices for manipulation and storage of information encoded in the spin degree of freedom of carriers. The crucial requirements for successful implementation of computational algorithms in spintronic devices are high mobility, sufficiently long spin coherence length and means of control of the parameters of the underlying hetero-structure. Thanks to the unique band structure of graphene, namely the two Dirac cones describing the low lying excitations, the above conditions are met in the recently fabricated devices. Most notably in the high quality graphene based devices created in the team of our collaborators Liyuan Zhang, Jorge Camacho, Igor Zaliznyak, Tonica Valla, and Myron Strongin in Brookhaven National Laboratory. The collaboration with the above group proved to be useful and essential for the project. The theoretical understanding of spin dependent transport requires the detailed analysis of the passage of spin carriers through the regions with varying magnetization. In our research we studied theoretically the transition of the spin carriers through the domain wall.

The samples fabricated in Brookhaven National Laboratory are characterized by exceptionally long mean free path of the order of few microns and are essentially ballistic. For that reason we employed the Landauer approach to treat the spin dependent transport in the graphene based hetero-structure.

Technical Progress and Developments:

In the framework of Landauer transport theory the conductance is determined by the transition probability of the carrier propagating from the source terminal to the drain terminal across the domain wall. As the spin carrier experiences the time dependent magnetic field inside the domain wall the passage may lead to flip of the spin polarization. It is important to calculate the probabilities of passage through the domain wall for all conducting channels and the relevant range of gate voltages.

Here we present the probability of the passage through the wall for thin (Fig.1) and thick (Fig.2) domain walls as a function of the angle of incidence. In both cases the solid curve corresponds to no spin flip events and the dashed line indicates the spin flip probability

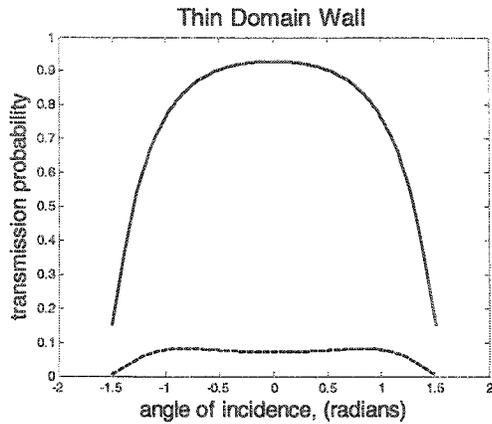


Fig.1

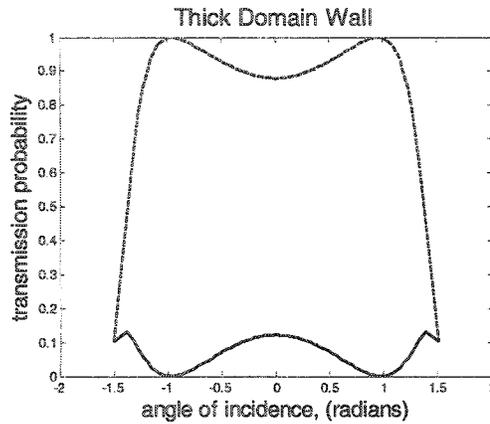


Fig.2

The calculation of the *spin-dependent* conductance is an important milestone of the project. This conductance physically corresponds to two-terminal measurement with ideal contacts under the spin selective bias. Here we present graphically the resistance of the device when the source and drain terminals have opposite polarizations (dashed line) and when the two polarizations are identical (solid line). The results are presented for the thin (Fig. 3) and thick (Fig. 4) domain wall.

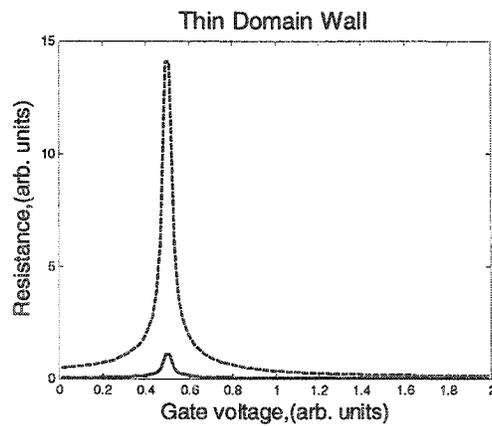


Fig.3

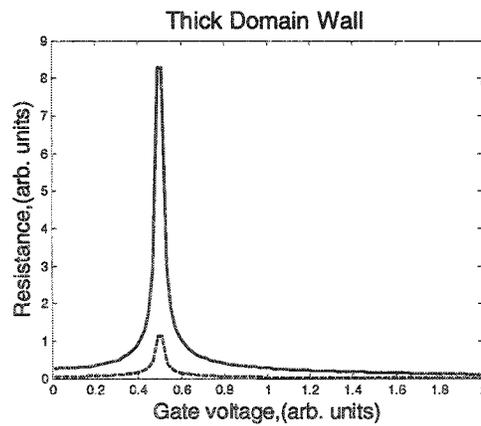


Fig.4

Getting to Know Your Constituents: Studies of Partonic Matter at the EIC

LDRD Project 08-004

Werner Vogelsang

PURPOSE:

The goal of this LDRD is to develop and commission an operational framework for the extraction of the distributions of quarks and gluons, the elementary particles of the strong interactions in nature, inside nucleons and atomic nuclei from future data taken at an Electron-Ion Collider (EIC). The expected main technical result of the work pursued in this LDRD will be an extensive computer (Fortran) code that will allow to perform sensitivity studies for quark and gluon distributions in future EIC measurements. The code is expected to help determine the optimal choices for the collision energies and detection capabilities at an EIC and would therefore be an essential part of the preparations for this machine.

APPROACH:

The EIC, with its unique assets of high energy and availability of polarized and nuclear beams, will be the ideal place for investigations of the quark and gluon (or, “parton”) sub-structure of nucleons and nuclei. Other lepton scattering experiments, as well as RHIC, are presently already providing information and will continue to do so in the pre-EIC era. In making the science case for an EIC, it is therefore important to assess the impact that EIC measurements would have. This is also closely tied to the developments of the optimal design of an EIC. This need for detailed early studies is the background for the present project. The specific implementation of analyses of quark and gluon distributions in polarized nucleons and in nuclei and their application to the needs at an EIC had not been achieved so far.

Our investigations are being done in a staged approach. Stage 1 is the development of the global analysis technique and its benchmark application to RHIC data. This serves as a proof of the concept and feasibility of the project. We are currently still in this stage and have made very significant progress toward its completion. Stage 2 foresees the incorporation of simulated EIC data into the analysis, followed by studies of sensitivities to the quark and gluon distributions at the EIC. Finally, in Stage 3 we plan to identify the requirements for energies and detectors at the EIC, and to further apply the results of the earlier stages. This outlines the scope of our investigations.

The main technical method we are using to carry out the work is a mathematical approach known as “Mellin technique”. This technique allows to incorporate all presently available data, as well as projected (or actual) future EIC data in a combined analysis at “next-to-leading order” of QCD. The actual analysis can then be done in terms of a χ^2 analysis of all data. This also includes a proper treatment of the experimental and theoretical uncertainties and their impact on the extracted quark and gluon distributions.

The co-investigators on this LDRD project are A. Deshpande (Stony Brook) and R. Milner (MIT) (for the parton distributions of the nucleon) and D. Kharzeev and R. Venugopalan (BNL) (for studies of the structure of nuclei). We decided to choose a somewhat unusual “strategic” approach for realizing the goals of this LDRD. Rather than hiring a postdoctoral researcher for the duration of the project, we only do a part-time contract hire and use the remaining funds for attracting more senior visitors for short and/or long-term visits to the laboratory. This appears to us to be the optimal approach. The project we are working on needs expert input at many levels, ranging from theoretical/mathematical background to high-performance computing and code

development, treatment of experimental and theoretical uncertainties, and so forth. This is best provided by a group of experienced researchers who devote part of their time to the project. It is still important to have a collaborator at the postdoctoral level at certain times of the project, performing some of the detailed studies and computer implementations of the method. We have chosen Swadhin Taneja for this role, who is currently a postdoc at Stony Brook University. Dr. Taneja has a unique background in both theoretical and experimental physics. We have recently hired him on a contract basis, initially for four months (beginning 09/2008). In addition, we have had short-term visits by M. Stratmann (RIKEN) and D. de Florian (Buenos Aires U.) who are experts in analysis techniques for nucleon and nuclear quark and gluon distributions. A long-term visit by Dr. de Florian is currently ongoing. We also had visits by A. Bacchetta (Jefferson Lab) and A. Mukherjee (Mumbai), for exploratory discussions about the dependence of the parton distributions on transverse momentum. LDRD funds have also been used for travel of the PI to a workshop on the EIC in Trento/Italy, and for purchase of computers used in the analysis.

TECHNICAL PROGRESS AND RESULTS:

Fiscal year 2008 was the first year of funding for this project. We have made very significant progress since the official start on 01/2008. We have realized a large part of Stage 1 (see above). One sample result is presented in the figure, which shows the spin-dependent gluon distribution of the proton, as a function of momentum fraction, as extracted from RHIC and other data. This

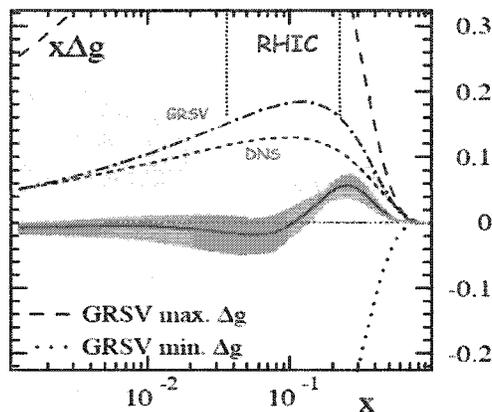


Fig.1: Spin-dependent gluon distribution Δg as function of gluon momentum fraction x , extracted from RHIC and DIS data. The green and yellow bands are measures of the present uncertainty. The region of momentum fraction covered by RHIC is indicated, and results of earlier analyses (“GRSV, DNS”) prior to RHIC are shown for comparison. Published in D. de Florian et al., *Phys. Rev. Lett.* **101** (2008) 072001.

analysis involved preparation of a Fortran code implementing the Mellin method and χ^2 analysis. As a scientific result, the analysis indicates that the spin-dependent gluon distribution in the proton is relatively small, and that large contributions by gluons to the proton spin are not likely. This result by itself will influence the plans for an EIC. Our current efforts aim at completing Stage 1 by improving the analysis of the uncertainties of the extracted parton distributions. This work is done in part by S. Taneja, and also by M. Stratmann. Dr. Taneja has in addition performed extensive comparisons of codes provided by other groups in the field, which will provide important cross-checks for the correctness of our analysis code. Completion of Stage 1 also involves implementation of our technique to nuclear parton distributions, which has not been performed yet. This will be one milestone for the next year. The other milestones for the next two years of funding will be the completions of Stages 2 and 3 (see above). Dr. Taneja is now in the process of preparing Stage 2, by simulating data and their uncertainties expected at an EIC. These will subsequently be used as input for the analysis code, in order to investigate what impact the EIC will have on our knowledge of the structure of polarized nucleons and of nuclei.

Development of the Deuteron EDM Proposal

LDRD Project 08-005

Yannis Semertzidis

PURPOSE:

To develop a sensitive storage ring electric dipole moment (EDM) experiment capable of probing the EDM of the deuteron and proton at the 10^{-29} e-cm level. At this level they will probe new physics at the 300~TeV mass scale, or if there is new physics at the LHC scale (~1TeV) they will probe CP-violating phases at the 10^{-5} rad level, an unprecedented sensitivity level. If a non-zero EDM value is found, it will help explain the baryon asymmetry of our universe (BAU).

The experiment that will result from this development will be launched at the AGS experimental floor and will use BNLs capability and experience with high intensity polarized beams. The deuteron and proton EDMs will provide a new program (facility) for probing the EDMs of charged particles directly. This current LDRD supports the development of a high efficiency with high analyzing power and very low systematic errors. Currently the testing of the polarimeter concepts is taking place at COSY near Juelich in Germany.

APPROACH:

Our collaborator Dr. Edward Stephenson from IUCF is the world's expert on hadronic polarimeters and he is the team-leader of this effort. Our goal is to achieve a polarimeter of at least 1% efficiency, analyzing power of about 40%, and systematic error of less than 10 parts per million (10 ppm) for early to late measurement during the 10^3 s of storage time. We are using the storage ring at COSY, where polarized deuterons are currently available, for development and testing the concepts. For the needs of the tests we have retrofitted a segmented detector located at the COSY ring. We have used computer simulations to optimize the efficiency of the detector and its analyzing power as well as minimize the systematic errors.

We intend to minimize the systematic error by a number of techniques based on data. We will be testing the models we have developed at the scheduled runs at COSY.

We have also developed the data acquisition needed to take the required data. For every year's running time at the storage ring we are required to submit a proposal and a report at the end of each run to the COSY PAC. The funds were allocated according to:

TECHNICAL PROGRESS AND RESULTS:

We had two significant runs: one in June 2008 of about two weeks and one in September 2008 for again about two weeks. We have devised an efficient method of extracting the deuteron beam onto a solid carbon target where they undergo nuclear elastic scattering. At this point we have achieved to take significant data to show that the detector efficiency is about 0.1% and the average polarization better than 50% consistent with the simulations.

We have also developed a process to minimize the systematic errors for which we have preliminary (and promising) results.

We were also able to flip the deuteron polarization during storage and monitor this polarization with our polarimeter in real time.

We have also demonstrated 1000ppm early to late stability (statistics limited) during our September 2008 run.

For the current year (FY2010) we expect to achieve 50ppm early to late stability demonstration (statistics limited). In order to achieve the goal of 10 ppm we need to develop a more efficient data acquisition system as well as a more efficient detector system.

Dr. Astrid Imig and Dr. Vasily Dzhordzhadze have been hired as post docs to work on the project. Dr. Imig has a PhD on deuteron polarimeter and extensive experience on hadronic polarimeters.

Dr. Dzhordzhadze is a software expert who has simulated the polarimeter detector in the process of optimizing it. The LDRD pays for all the travel of all the members of the collaboration from the US. Europeans pay their way to Germany for the tests and the detector development.

We will be having a technical review in fall 2009 (initiated by Steve Vigdor) and a significant part of it will be the questions addressed by this LDRD.

For FY2009 we expect to achieve 50 ppm of stability demonstration from early to late storage times.

For FY2010 (only partially funded so far) we expect to reduce this error significantly. Additionally we expect to make measurements related to the work of spin coherence time to calibrate the simulation programs we are currently developing.

Development of Small Gap Magnets and Vacuum Chamber for eRHIC

LDRD Project 08-008

Vladimir N Litvinenko

PURPOSE:

The Development of small gap magnets and vacuum chamber compatible with multi-pass energy-recovery linac has high potential of being a cost effective solution for eRHIC using RHIC tunnel for its five return loops (see Fig. 1). Using RHIC tunnel is only viable option of operating eRHIC with electron energies above 10 GeV. Inexpensive 3.8 km long loops are essential for reducing the size and the cost of super-conducting RF linac and the eRHIC's cost.

- Small gap provides for low current, low power consumption magnets
- Magnetic design - W. Meng, mechanical engineering - G. Mahler

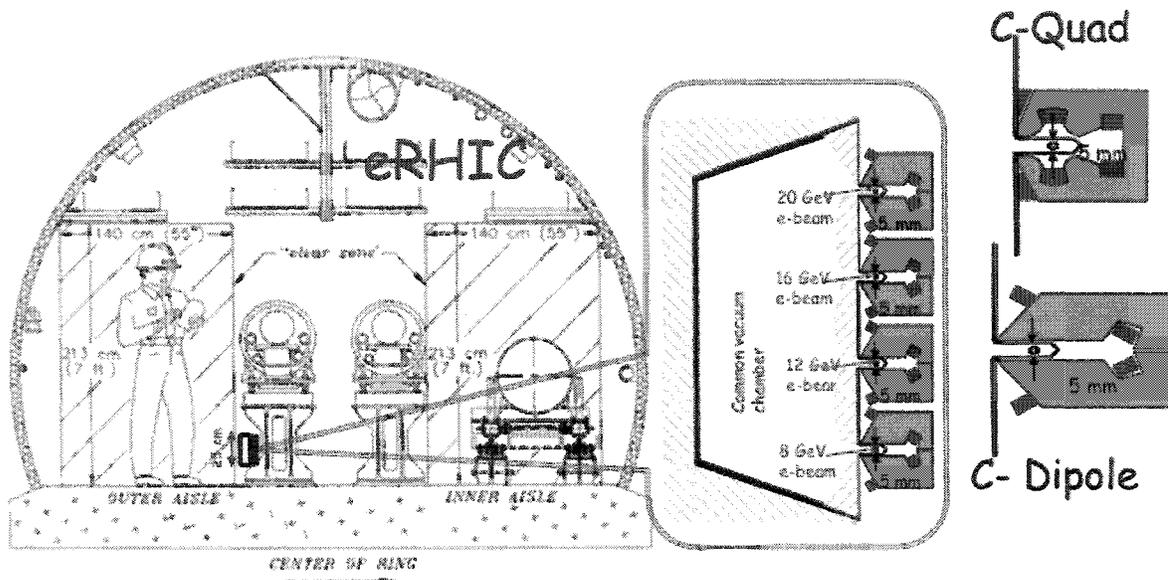


Fig.1. Concept of multi-pass vacuum chamber

The motivation of this research is twofold: First, demonstrate that a small gap magnets and multi-pass vacuum chamber can be manufactured to satisfy specs for eRHIC. Second, demonstrate that such components will provide sufficient operational margins (i.e. tolerance to errors in field and alignment) for eRHIC.

APPROACH:

Using ERL for eRHIC provides electron beam with very small emittance and as the result as with very small sizes. In return, it allows one to design loop magnets for eRHIC with very small gaps (few millimeters) and install them at a single vacuum chamber. The main goal of this research is test of the viability of this concept, including studies of the quality of magnetic fields in prototype dipole and quadrupole magnets, stresses and deformation of thin-wall convolutions of the vacuum chamber. Small gap of the magnets allow using low-current coils with low power consumption. Such magnets will be also low weight and inexpensive. Overall, such design allows one to reduce energy gain in the ERL linac and to increase number of the loops.

The technical challenges are:

- the C-shape magnets with limited extend towards common vacuum chamber should provide field quality necessary for beams stability and beam quality preservation in high luminosity eRHIC;
- the common vacuum chamber with multiple mini-chambers sticking out into mini-gap magnets should not sag and must provide sufficient aperture for high intensity electron beams.

This challenges are addressed by designing, manufacturing and measuring one prototype of each component for the eRHIC loops.

The scientific challenges are:

- design eRHIC loop lattices which are tolerant to the level of magnetic field errors and harmonic content characteristic for such small aperture C-shape magnets with limited extent - this include but is not limited to design of orbit correction scheme for eRHIC;
- evaluation of the beam dynamics in eRHIC in the presence of expected errors in magnets and setting specifications for expectable errors the fields, positions and angles.

TECHNICAL PROGRESS AND RESULTS:

Magnetic design: Magnetic designs are developed by Dr. Wuzheng Meng in consultation with the PI and project engineer George Mahler. During this research period we made two magnetic designs of the dipole magnets and two magnetic designs of the quadrupole magnet (Fig.2).

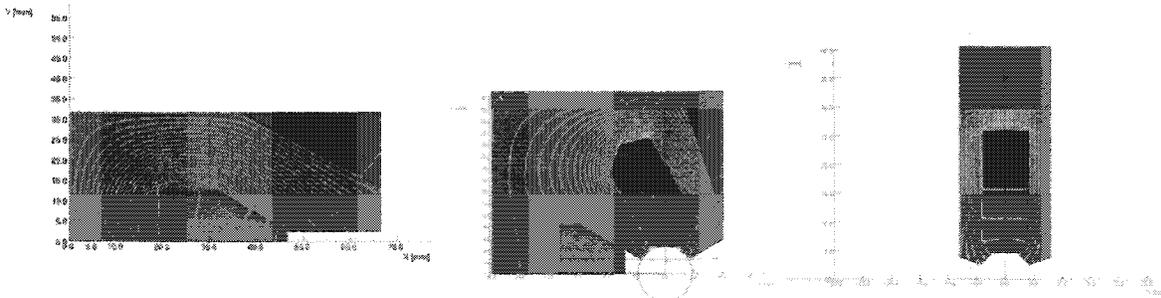


Fig.2 Design of the dipole magnet (left) and two designs of the quadrupole magnet (ver. 1 – center and ver.2 – right) with total gap of 5 mm.

Quality of the magnetic field was evaluated and the designed field quality of the dipole magnet was found adequate (Fig.3). Non-linear deviation of the magnetic field within designed aperture (± 3 mm around the 10 mm mark, which coincides with the center of the beam) is less than ± 0.05 Gs, $\frac{\Delta B}{B} \leq 2 \cdot 10^{-4}$. The same is true within ± 2.5 mm of vertical gap. Even ± 4 mm radial aperture seems to be feasible (to be confirmed by simulations). This design promised to be adequate and we proceeded with the prototyping of this magnet (see next section).

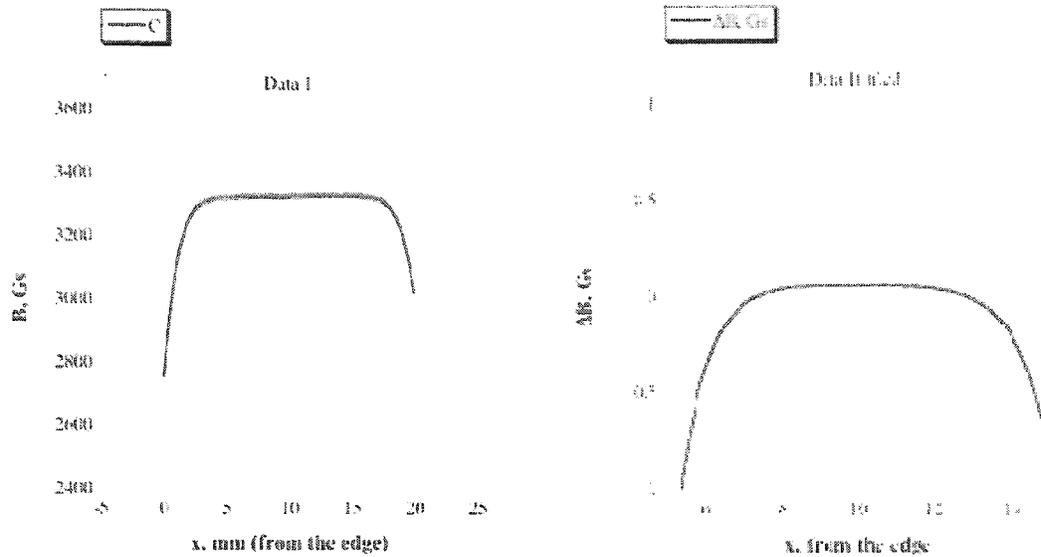


Fig.3. Radial profile of the designed vertical component of the magnetic field in the eRHIC dipole: Total field – left, nonlinear component of the field – right. The mark 10 mm corresponds to the e-beam axis in the chamber. Edge of the dipole magnet is located at 0 mm.

Two designs of the quadrupole had been studied and there is a clear path to optimized design. Magnetic design of quadrupole with desirable quality of the field is in progress and will be finished within 3 months.

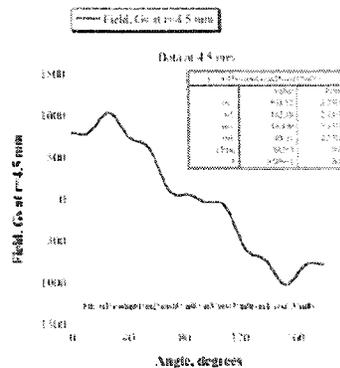


Fig.4. Magnetic field of the ver.1 quadrupole at 4.5 mm radius. There is significant component of harmonics (non-linearities) in the field.

Mechanical design and prototyping: Mechanical designs of the dipole magnet was developed by George Mahler. First solid 45-cm long prototype of the dipole magnet with 5 mm total gap was manufactured at BNL central shop using EDM (Electric Discharge Machining) technique(see Fig. 5). We plan also to use an alternative grinding technique for another prototype comprising of 2 halves of the core which will be precisely pinned and bolted together. The coils for the magnet had been designed and being manufactured. The magnet would be assembled and go through magnetic measurements as soon as coils are in hand.

The same processes will be repeated with the quadrupole magnets.

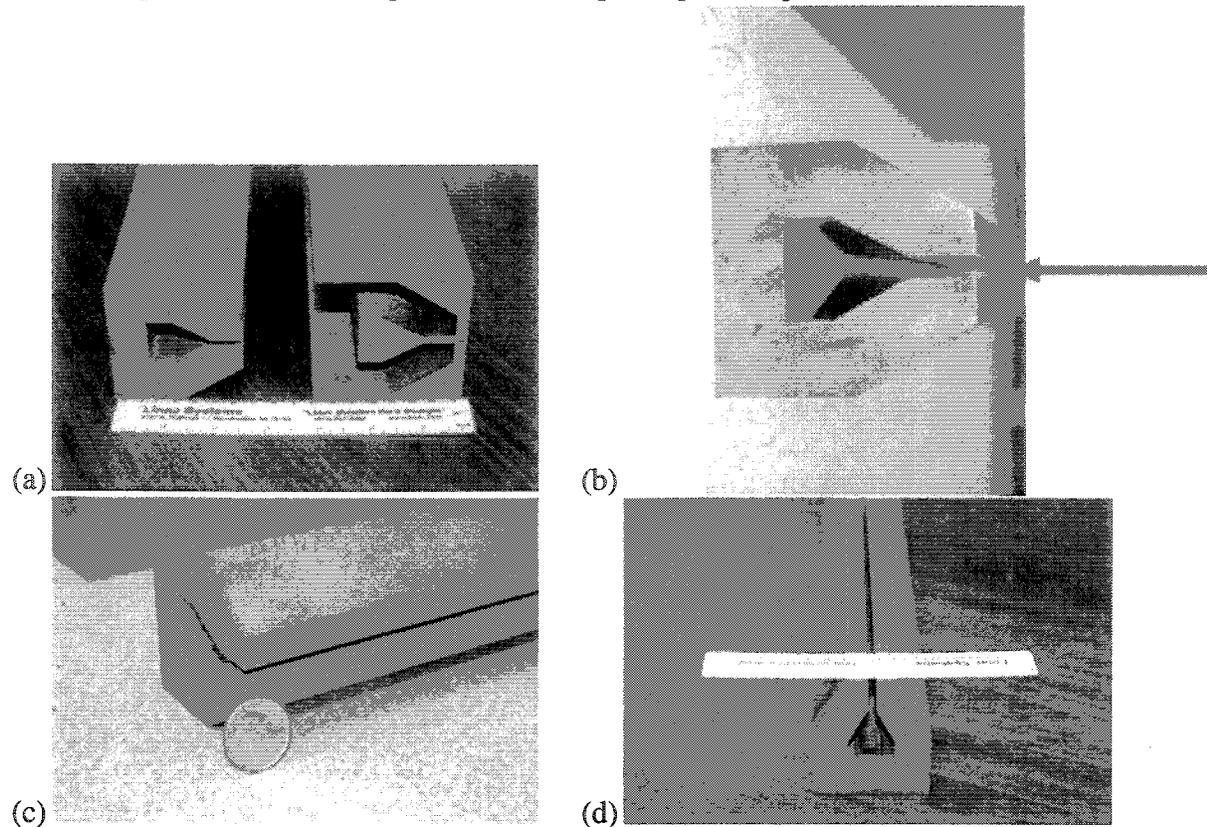


Fig.5. The 45-cm long dipole magnet core was made from 3" x 3" magnetic steel chunk using EMD technique. Fig (a) shows the dipole core and its "negative" replica. Figs (b-d) show various views of the core, with blue arrow pointing to 5 mm magnetic gap.

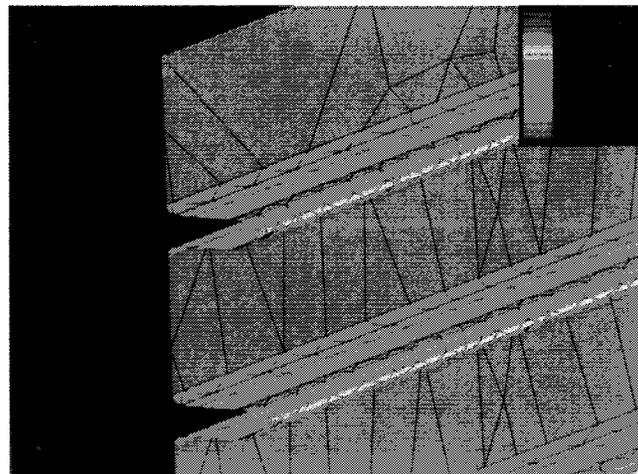


Fig.6. ANSYS simulations of the multi-passage vacuum chamber

Mechanical design of the Al vacuum chamber with four individual beam-passages is in the progress. ANSYS simulations (see Fig. 6). showed that use of 0.03" thickens of Al wall for the passages (convolutions which go inside the magnets) is sufficient: both the stresses (at 1400

level) and the walls displacement of 3.5 micron (max) under atmospheric pressure are acceptable. The prototype will be designed and manufactured in 2009.

Particles tracking in multi-pass ER: the simulation of the particle motion will be performed by newly hired post-doc, Yue Hao, in collaboration with Johan Bengtsson (author of Tracy II code, from NSLS II team). The goal of this studies is to determine the tolerances for magnet filed errors and magnet alignment errors. We will use Tracy III tracking code, which is modified by Dr. Bengtsson for multi-pass ERLs. The code is undergoing the tests and studies will be completed in 12 months.

TIMELINE for FY 2009:

1. **Dipole:** we plan to assemble working dipole in March, 2009 and test it performance. A second prototype tests are contingent on the results of the first prototype.
2. **Quadrupole:** we plan to finish magnetic design of quadrupole in February, 2009 and to have a prototype manufactured by May. We plan to test the quadrupole in August 2009.
3. **Vacuum chamber:** we plan to finish design of the chamber in January, 2009, manufacture it in March, 2009 and test it in May, 2009.
4. **Tracking:** Tracking studies will go into next FY and will be completed by the end of the project in late 2009.
5. **Contingencies:** we have contingency plans (different materials or/and manufacturing techniques) if one of the prototypes fails.

Novel Methods for Microcrystal Structure Determination at NSLS and NSLS-II

LDRD Project 08-022

Allen M. Orville, Alexei S. Soares, Howard R. Robinson and Annie Héroux

PURPOSE:

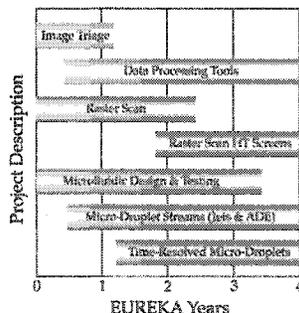
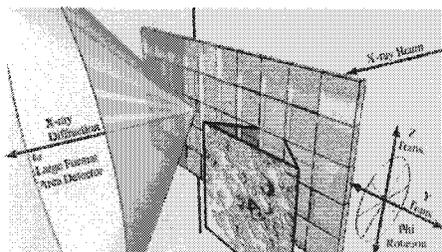
The frontier of structural biology is defined, in part, by the structural analysis of membrane proteins, large macromolecular complexes of proteins and/or protein-nucleic acids, and whole virus particles. Unfortunately, the complexity of these systems frequently limits the availability of large, single crystals. In contrast, microcrystals measuring only a few microns along an edge are often easy to obtain even from these systems; but they are difficult to use because they are too small to yield a suitable diffraction pattern with conventional macromolecular crystallography (MX). Therefore, a major barrier that remains to be overcome in MX is how to manipulate microcrystals for structure determination. This is especially true at existing third-generation synchrotron X-ray sources and for the NSLS-II under construction at Brookhaven National Laboratory. This new source, and indeed all third generation sources, requires either significant attenuation of the X-ray beam, or radically new methods of data collection to prevent radiation damage within several milliseconds of exposure. This proposal addresses these critical gaps.

APPROACH:

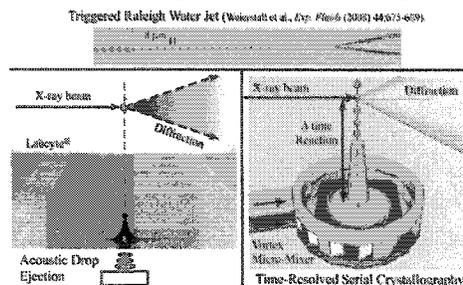
Our plan is to use a statistically large number of randomly oriented microcrystals for high throughput crystal structure determinations. We believe that our results will push back the frontiers of structural biology research highlighted above, as well as establish time-resolved crystallography as a generally applicable technique for the first time.

Research Plan: The essence of our plan, termed “Serial Micro-Crystallography”, is to use a statistically large number of randomly oriented microcrystals. Each will be taken potentially to the X-ray radiation dose limit with highly-focused, unattenuated X-ray beams. However, only a small fraction of the whole dataset will be collected from each microcrystal. Consequently, the complete dataset will be built-up serially from many narrow slices of reciprocal space. Although each dataset will derive from a large number of microcrystals, each microcrystal will experience relatively little manipulation during the data collection. As a result, we envision that our methods will also be very high throughput. As illustrated on the next page, we are following two parallel strategies to collect X-ray diffraction data from microcrystals: A) Raster-Scan, and B) Micro-Droplet Stream. In the first strategy the X-ray beam is scanned in a logical raster pattern across a support grid containing a microcrystal slurry. In the second strategy, a stream of microdroplets is created from a microcrystal slurry such that each drop contains one microcrystal on average. The droplets will traverse the X-ray beam one by one, and those containing a crystal will yield a diffraction pattern. We are currently designing microfluidic devices to deliver the microcrystal slurry to either the raster-scan grids or to create the microdroplet streams. Because structure and function are linked fundamentally, another frontier aspiration of many biochemists and structural biologists is to determine molecular movies of enzymes engaged in catalysis. In our most ambitious plans, we will fabricate a novel microfluidic, vortex micromixer immediately upstream of the droplet nozzle. This will provide a means to introduce known delta-time intervals appropriate for most catalytic reactions, and thus enable time-resolve serial micro-crystallography. Most importantly, for the first time this technology will be truly general.

Raster-Scan Concept



Micro-Droplet Stream Concepts



TECHNICAL PROGRESS AND RESULTS:

Dr. Marc Allaire and his graduate student, Mr. Matthew A. Engel (enrolled in the Biomedical Engineering Program at SUNY-SB), joined the collaboration recently. They are focusing on methods related to the Raster-Scan research objectives at beamline X25.

The general concepts of the LDRD proposal at their current stage of development are illustrated above. The graphic was adapted from the most recent grant proposal that Drs. Orville, Allaire, and Soares submitted to the NIH on October 28, 2008. The particular metrics for the EUREKA proposal are listed in the LDRD Data Collection Form. The anticipated timeline for the major focus areas of the four-year project is outlined in the central portion of the figure above. The new EUREKA proposal will also draw in collaborations with scientists at the BNL Center for Functional Nanomaterials (CFN) and a data processing specialist affiliated with the Diamond Light Source in South Oxfordshire, Great Britain.

We have produced microcrystal showers of several well-known standard proteins including lysozyme, insulin, taumatin, and nitroalkane oxidase. The photomicrograph inserted into the figure on the left above shows a lysozyme microcrystal slurry sandwiched between layers of x-ray transparent tape. Allaire and Engle have demonstrated diffraction from slurries of this type. Custom 2D arrays are being designed and fabricated in collaboration with the CFN. The raster scan methods are under investigation at X25.

We are commissioning the Crystal-Logic micro-diffractometer at beamline X25. It is well suited to the Raster Scan methods because it has an X,Y,Z translation accuracy of less than one micron and a 0.125 μm radial/axial error motion. In addition, the single-bounce, focusing Bilderback capillary is also currently undergoing commissioning at X25. We have recently observed an x-ray beam with $\sim 35 \mu\text{m}$ horizontal (FWHM) by $\sim 25 \mu\text{m}$ vertical (FWHM) dimensions, with about 3-5 mrad of beam convergence, and $\sim 4\text{-}5\text{x}$ gain in x-ray beam intensity.

We are designing and will test three methods to generate the Micro-Droplet Streams as illustrated above: i) triggered Raleigh water jet, ii) acoustic drop ejection (ADE), and iii) time-resolved serial crystallography. We have a new collaboration with LabCyte® to test ADE technology for serial crystallography. In collaboration with the CFN here at BNL, we are designing and will fabricate the novel microfluidic devices to support time-resolve serial crystallography.

Combined PET/MRI Multimodality Imaging Probe

LDRD Project 08-025

David J. Schlyer

PURPOSE:

The goal is to design a multimodal imaging probe for use with our combined MRI-PET animal imaging system which will allow simultaneous PET and MRI measurements. The probe will contain both a positron emitting radionuclide and a superparamagnetic MRI contrast agent in a single iron oxide nanoparticle. There is mounting evidence that most disease processes can be identified by altered molecular profiles and/or cell behavior prior to visual anatomic alterations. Insight into these processes could potentially allow for (1) the early detection of disease, (2) more accurate prognoses and personalized treatments, (3) the ability to monitor the effectiveness of therapeutic treatments, and (4) improvements in our understanding of how cells behave and interact in their intact environment in living subjects. This dual probe concept combines the strengths of both PET and MRI into a powerful new tool for quantitative molecular imaging.

Expected Results: Our specific aims are to:

1. incorporate a positron emitting radionuclide into superparamagnetic iron oxide nanoparticles,
2. attach specific biologically active molecules to these nanoparticles,
3. perform simultaneous PET/MRI on these particles as a research and potential diagnostic tool for medical imaging and to map localization as a potential radiotherapeutic agent.

When these specific aims are accomplished, we expect to be able to show simultaneous imaging of the probe with both PET and MRI with specific localization based on the biological probe attached. We expect to be able to prove the utility of this approach and have enough preliminary data for submission of a grant application to NIH.

APPROACH:

Molecular imaging with PET has already had a profound effect on our understanding in both preclinical and clinical areas including cancer research and many aspects of neuroscience from cognition to psychiatric diseases. MRI is beginning to move from structural and functional imaging to molecular imaging, but this is in the early stages and requires considerable development. The combined use of PET and MRI with our proposed imaging agents could be a quantum leap forward in synergistically addressing problems of cellular pathophysiology. One key advantage of this approach is that the radionuclide probe is included in the nanoparticles which means that the radionuclide will stay with the nanoparticles as opposed to some other radiolabel nanoparticles in which the radionuclide is attached to the nanoparticles using a chelating agent which may release the radionuclide under biological conditions.

We will address each of our specific aims in the following ways:

Specific Aim 1 - Incorporate Iron-52 in Nanoparticles: Superparamagnetic iron oxide (SPIO) MR imaging contrast agents consist of an iron oxide nanoparticle core covered with a coating material (such as dextran). They can also be easily incorporated into cells. A diagram of the envisioned probe is shown in Figure 1.

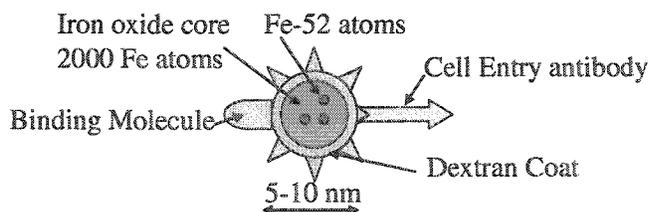


Figure 1. Schematic diagram of the radiolabeled nanoparticle molecular probe

The goal is to prepare magnetic particles doped with a radionuclide. For instance, spinel ferrites with a general formula MFe_2O_4 where $M = Mn, Co, Ni, Cu, Zn, Mg, \text{ or } Cd$, can be synthesized by microemulsion technique in the lab with controllable sizes of 4-15 nm. Such a nanoparticle would then be coated with either dextrane or phospholipids to reduce agglomeration. The labeling with biologically active molecules will be done in collaboration with the Center for Functional Nanomaterials (CFN) at Brookhaven National Lab (BNL) and the BNL Medical Department radiochemists.

Specific Aim 2 - Attach Specific Molecules to the Nanoparticles: A variety of biological molecules have been attached to these nanoparticles and used both in vitro and in vivo. To date, studies have shown that the polymer-coated nanoparticles have minimal impact on cell viability and function.

Specific Aim 3 - Use Simultaneous PET/MRI: We have developed a scanner that will allow the simultaneous acquisition of quantitative physiological data using PET, and high resolution anatomical or even complimentary functional data using MRI (4).

TECHNICAL PROGRESS AND RESULTS:

- All Experimental Safety Reviews and Radiation Work Permits have been written and approved. Permission to proceed with the experiments has been obtained.
- The preliminary chemistry has been carried to produce the nanoparticles and in-house characterization has been established
- Commercial nanoparticles of the same chemical composition have been purchased and are being tested for sensitivity on the 4T MRI scanner
- The commercial particles have been characterized using the facilities of the Center for Functional Nanomaterials (CFN).
- The same methodology has been used to characterize the unlabeled nanoparticles produced in the laboratory
- The radionuclide production chemistry for F-52 has been reviewed and is being adapted to the BLIP

Experiments are underway and we hope to have preliminary results within the next few month. Our milestones for the next year are:

- Finish the sensitivity measurements of the commercial nanoparticles
- Compare the sensitivity in the MRI for the nanoparticles produced in the laboratory using phantoms
- Radiolabel the nanoparticles and perform aggregation measurements to determine the rate of aggregation

Genomic DNA Methylation: The Epigenetic Response of *Arabidopsis Thaliana* Genome to the Long-Term Elevated Atmospheric Temperature and CO₂ in Global Warming

LDRD Project 08-028

Qiong (Alison) Liu

PURPOSE:

The goal of this project is to determine the changes of DNA cytosine methylation in genome of *Arabidopsis* plants in response to elevated temperature and CO₂ levels such as would occur during global warming. This epigenetic information will help us to understand temperature and CO₂ regulated plant developmental and flowering pathways, and the regulation of small RNA and DNA methylation and their involvement in plant adaptation to environment. To achieve this goal, we are employing newly developed assays for detecting DNA methylation.

APPROACH:

Exponential emission of CO₂ into the atmosphere resulted from human activities has led to an enhanced greenhouse effect or global warming. Prolonged increase of temperature has been shown to increase the growth rate and induces early flowering of plants in laboratory experiments (Balasubramanian S. et al. PLoS genetics. 2006 2(7): 980-9), and correlated to biomass and grain reduction in crops (Peng S. et al. Proc Natl Acad Sci U S A. 2004 101(27): 9971-5). Paleobotanical evidence has linked a fourfold increase in atmospheric carbon dioxide and an associated 3° to 4°C greenhouse warming to a well-documented major faunal mass extinction during the period of Triassic-Jurassic boundary (McElwain JC et al. Science 1999 285: 1386-90). Some prior evidences suggest that plants may respond to altered temperature and CO₂ level via an epigenetic response. For example, microarray studies have identified many gene expression changes in *Arabidopsis* when the plant is grown at a few degrees higher temperature (Balasubramanian S. et al. PLoS Genetics, 2006, 2(7);980-9). A few small RNAs are also generated or altered in *Arabidopsis* growing at a lowered temperature (Oh M. et al. Journal of Plant Biology, 2007, 50(5);562-67).

We have initially grown *Arabidopsis* plants at 22°C, 26°C, and 28°C, and at 400ppm and 800ppm CO₂ concentration. We are using improved LUMA assay to analyze the overall genomic DNA methylation, and are working on a better unbiased method for the same purpose. We are analyzing the overall genomic DNA methylation level of these plants through the deep sequencing of small RNAs, which regulate genomic DNA methylation in their hybridization sites on genome. We are also working to profile the genomic DNA methylation in these plants using methylated cytosine immunoprecipitation in combination of an Affymethix *Arabidopsis* tiling array, and are working towards the single nucleotide resolution of cytosine methylation profiling of genome using new generation sequencing method.

For this project, Alison Liu has collaborated with (1) Alistair Rogers at Environmental Science at BNL to obtain the *Arabidopsis* plants grown at FACE condition at Oak Ridge, Tennessee, (2) with Deng's lab at Yale University for growing *Arabidopsis* plants at different temperatures, (3) with Cold Spring Harbor Laboratory Genome Research Center for sequencing small RNAs using Solexa sequencing facility, and (4) with Dr. Hengmi Cui at the Epigenetic Center at Johns Hopkins University for using their pyrosequencing facility for the improved LUMA assay.

TECHNICAL PROGRESS AND RESULTS:

This is a newly funded project, starting in March, 2008. The summarized results to date are as follow:

(1) **Plant growth:** *Arabidopsis* plants were grown in walk-in chambers at Yale University at 22°C, 26°C, and 28°C (Figure 1). The early induction of flowering time and enhanced hypocotyls elongation were observed in *Arabidopsis* at higher temperature compared to the lower one, agreeing with the previously published results. *Arabidopsis* grown at 28°C had smaller number of rosette leaves and their bolting time about 6-7 days earlier than those grown at 22°C. Rosette leaves of *Arabidopsis* plants grown at different temperatures were collected, and those grown at 400ppm or 800ppm CO₂ at 20-25°C between the end of summer and beginning of fall in a free-air CO₂ enrichment facility were harvested at 2-3 weeks old.

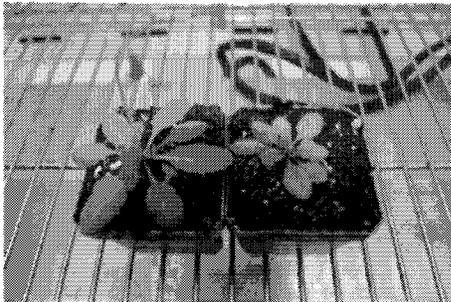


Figure 1. High temperature is a potent inducer of flowering in *Arabidopsis*. The plant on the left has been grown at 28°C, and the one on the right at 22°C. The pictures were taken three weeks after germination.

(2) **Gross evaluation of genomic DNA methylation in *Arabidopsis* grown at different temperatures:** using an improved version of LUMA assay, we have detected significant lower level of genomic DNA methylation in plants grown at 28°C, compared to those grown at 22°C. LUMA stands for LUMinometric Methylation Assay, and it was developed to determine dynamic changes in global methylation/demethylation events. It is a luminometric technology used to quantitate methylation sensitive restriction digestions (Karimi M et al., *Epigenetics*, 2006, 1(1);45-8). Using this method, we are currently testing more temperature related samples to further confirm this result, and those samples grown at the different CO₂ concentrations.

(3) ***Arabidopsis* small RNA deep sequencing.** Small RNA libraries were generated using *Arabidopsis* rosette leaves grown at 22°C and 28°C, and 400ppm and 800ppm CO₂ concentrations, indifferently by following Illumina small RNA preparation instruction manual (Figure 2.). 12 to 13 million sequence read were obtained in each library using Solexa sequencer at Cold Spring Harbo Lab. We are currently collaborating with Dr. Michael Zhang's lab at Cold Spring Harbor Laboratory to analyze these sequences. These results should reveal the new species of small RNAs, changes of the small RNA copy numbers among *Arabidopsis* grown under different temperatures and CO₂ conditions, and the genomic targeting sites for those small RNAs whose existence or expressions have been altered.

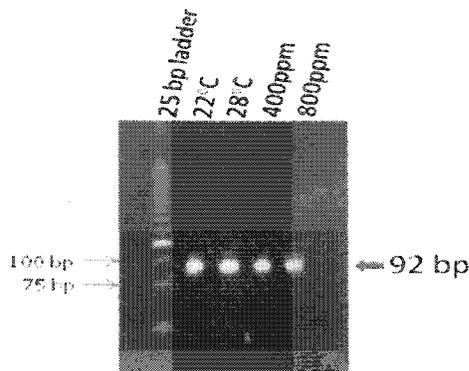


Figure 2. The small RNA libraries indicated on polyacrylamide gel. Small RNAs in size range of 18-30 nucleotides are purified, added with adaptors, and amplified. The average size of small RNA libraries is as indicated.

In summary, in the previous six months Alison Liu has generated plants materials and obtained the first evidence that higher temperature resulted in the significant reduction of genomic DNA methylation in *Arabidopsis* plant. A new *Arabidopsis* growth chamber has been purchased, and Dr. Hongli Zhai, a newly hired postdoc will join the effort in the coming year. We anticipate the full reveal of genomic DNA methylation changes of plants in response to different temperatures and CO₂ levels. Specifically, we will use a nonbiased method to quantify the gross methylation of plant materials, and determine the epigenome of *Arabidopsis* grown at different temperature and CO₂ using Affymetrix tiling array, high resolution sequencing in combination with bisulfate modification, and through small RNA sequencing method.

Fabry-Perot Interferometer & Hard X-Ray Photoemission

LDRD Project 08-034

Elio Vescovo

PURPOSE:

The purpose of this LDRD is to manufacture a Fabry-Perot (FP) etalon by micro-etching techniques on a single crystal Si wafer. The etalon has the advantage of easy construction, robust alignment and energy resolution below 0.1 meV. The etalon could be characterized combining two resonators in series and measuring the optical output of the system as a function of a temperature gradient between the two.

APPROACH:

Recently the feasibility of high-resolution FP resonators working in the hard x-ray region (~ 14 keV) has been demonstrated, using two single crystal of $\alpha\text{-Al}_2\text{O}_3$ separated by 50 nm and parallel aligned with very high precision (nanometer) [1]. A great simplification can be achieved by micro-etching the etalon on a single crystal Si wafer; the critical alignment between the two diffracting Si planes is therefore automatically guaranteed with atomic precision. The single piece interferometers is produced using the micro-etching facilities at the CFN and is tested at beam line X13B at NSLS.

TECHNICAL PROGRESS AND RESULTS:

First six months.

Dr. Yi Ding has been hired to work full time on this project.

We used deep reactive ion etching (RIE) technique available at CFN to fabricate the diffracting plates on Si wafers. Figure 1 shows a SEM image from one of our micro-structures: two cavities in series.

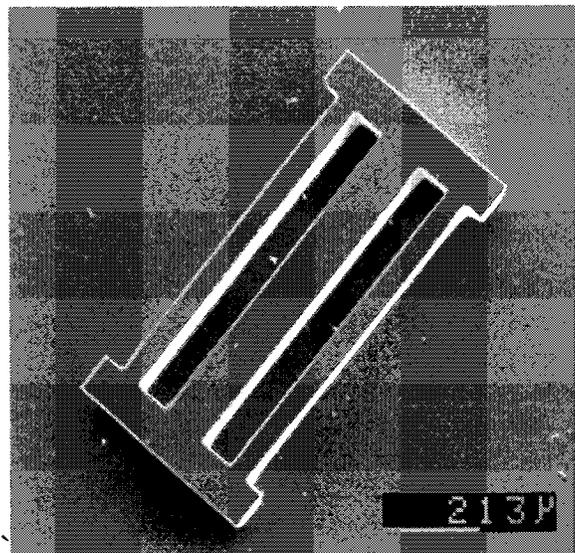


Figure 1: SEM image of two-cavity etalon.

The quality of these type of structures (particularly the lattice distortions at the walls, due to etching) can be characterized at beamline X13B using X-ray diffraction and a micro-focused beam. We initiated some of this work at X13B but found out that the present monochromator at X13B does not have the required energy resolution. We therefore proceeded to install an additional 4-bounces monochromator to improve the energy resolution. This operation is now close to conclusion. Figure 2 shows the (620) rocking curves of a piece of bulk Si crystal with

and without the additional (620) monochromator. We were able to improve the resolution from 9 arcsec to 3 arcsec.

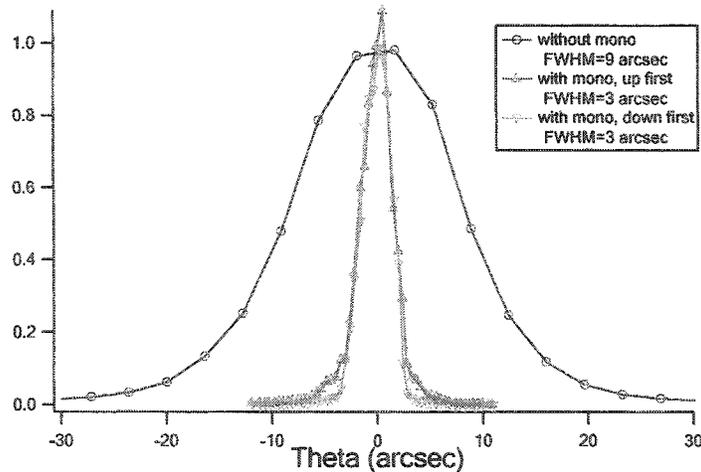


Figure 2: (620) rocking curves of a piece of bulk Si crystal with and without the additional (620) monochromator.

Figure 3 shows the (620) rocking curves of sample structure obtained via deep RIE, the Si wafer used to etch the structure, and a piece of bulk Si crystal. Within the 3 arcsec resolution we have right now, the etched structure showed no additional stress from the etching process.

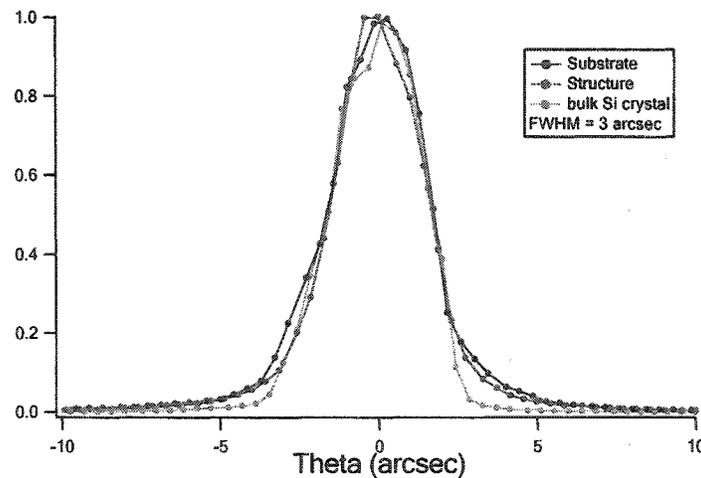


Figure 3: (620) rocking curves of sample structure, Si wafer, and bulk Si crystal.

Milestones for each year of anticipated funding.

First Year:

1. Hiring of a Postdoc to work full time on this project [Dr Yi Ding has been hired]
2. Manufacturing of single-wall and double-walls Si micro-structures from Si wafers [work partially accomplished]
3. Characterization via X-ray diffraction of the micro-etched structure [work in progress]

Second Year

1. Characterization of the etalon transmission; probably by measuring the output from a series of two identical etalons while varying the temperature of one of the two. This is expected to be a difficult task that will require to overcome many experimental difficulties.

REFERENCES

- [1] Y. Shvyd'ko et al., Phys. Rev. Lett. 90, 13904 (2003)

Ultrafast Electron Diffraction for Transient Structure and Phase Transition Studies at the NSLS SDL

LDRD Project 08-037

X. J. Wang, Y. Hidaka R. K. Li, C. C. Kao, J. B. Murphy, S. Pjerov and Y. Shen

PURPOSE:

Ultrafast electron diffraction (UED) is a promising technique that allows us to observe a molecular structure transition on the time scale on the order of femtoseconds (fs). Our goal is to design, optimize, and experimentally demonstrate a UED system with an atomic scale spatial resolution and a time resolution on the order of 100 fs, using an MeV electron bunch containing $\sim 10^6$ electrons. The specifications above give scientists an ability to take a “molecular movie” with significantly less data acquisition time than a conventional UED system using a keV electron beam. Once this objective is achieved, this system can be utilized by many users in a broad range of scientific fields to investigate the characteristics of samples of their interest. Brookhaven National Laboratory (BNL) would greatly benefit from the availability of this system on-site.

APPROACH:

UED has been continuously developed as a complementary technology to X-ray Free Electron Laser (X-FEL) for probing ultrafast events of ultra-small objects. UED has advantages over X-FEL in terms of its compactness, 10^6 times larger cross section, and less damaging ability to the samples investigated. Yet, the time resolution of conventional UED has been limited to over 1 picosecond (ps). It can be reduced to the order of 100 fs by decreasing the number of electrons in a bunch at the cost of reduced signal-to-noise ration (SNR), which requires multiple shots to obtain resolvable diffraction patterns.

One of the main causes for this limitation of UED is the space charge effect that prohibits a further compression of the probing electron beam bunch length. The other important limiting factor is the timing jitter mainly arising from RF to laser timing jitter and RF field amplitude jitter. Our study focuses on how to improve the time resolution by minimizing the adverse effects mentioned above, and to still maintain the desired spatial resolution and the number of electrons, i.e., the SNR.

To overcome this issue, we proposed to build a MeV UED system at the National Synchrotron Light Source (NSLS) Source Development Laboratory (SDL). Conventional UED employs subrelativistic electron beams in the range 30-60 keV. By increasing the electron energy to a MeV level, the space charge effect can be made negligible. Hence, an RF photoinjector with a high quality beam generation capability developed for FEL will be used as an electron source for our UED system.

TECHNICAL PROGRESS AND RESULTS:

The design of the proposed UED system has been optimized by tracking electrons from start (photoinjector) to end (detector), using both a particle tracking code PARMELA and a custom MATLAB code that calculates a scattering intensity distribution by an aluminum sample placed between the photoinjector and the detector. A sample diffraction pattern our simulation produced is shown in Fig. 1(a). From the pattern, we can plot the intensity of the diffraction rings vs. the radial coordinate, as shown in Figs. 1(b)-(d). It was found that decreasing the electron energy

increases the sharpness of the intensity peaks, which would give a finer spatial resolution, as indicated by Fig. 1(b). Decreasing the beam spot size and the beam divergence result both in sharper peaks, as shown in Figs. 1(c) and (d), respectively. The simulation results demonstrated that it is feasible to achieve 0.01 angstrom in spatial resolution and ~ 400 femtoseconds in temporal resolution for a MeV UED system, with the number of electrons in each bunch being 2 to 3 orders of magnitude higher than a competing keV UED system. The significantly increased number of electrons enables us to obtain single-shot diffraction patterns due to increased SNR. Even if a single shot does not yield a resolvable diffraction pattern, patterns from many shots can be accumulated to obtain a resolvable integrated diffraction pattern. In this case, more electrons require less shots, and hence less time for data acquisition.

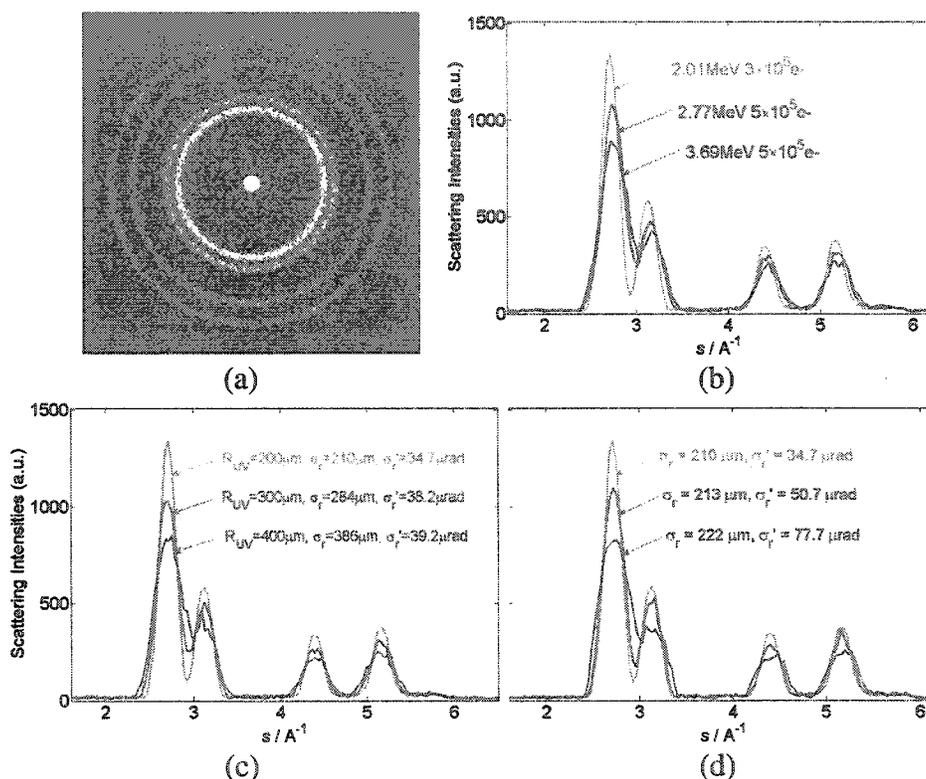


Fig. 1: (a) Numerically obtained sample diffraction pattern. Diffraction pattern intensity vs. radial coordinate, depending on (b) energy, (c) spot size, and (d) divergence of the electron beam.

Encouraged by the optimization discussed above, the MeV UED system at the NSLS SDL has been finalized as shown in the schematic in Fig. 2. Most major components in the system have been purchased or were already owned. Each component is currently under testing, and to be assembled and commissioned soon. In addition, the simulation model above is being reconstructed using GPT (General Particle Tracer) in order to run simulations with a single software from start to end.

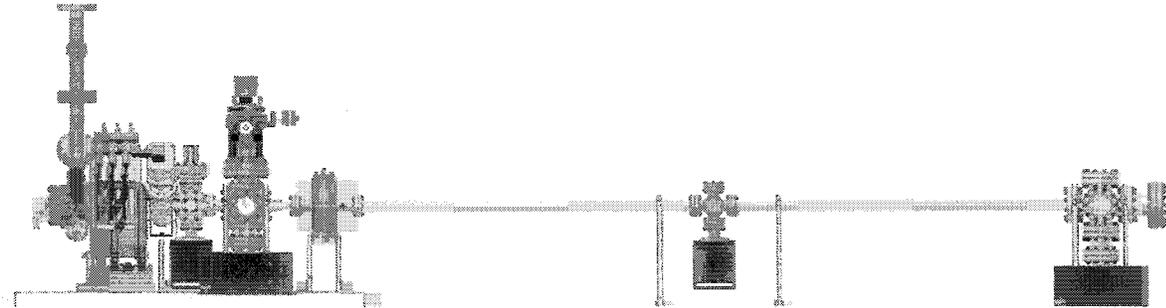


Fig. 2: Schematic of SDL NSLS MeV UED system.

Milestones for FY2009: May - First electron beam passing through the entire system; August - Obtain a clean diffraction pattern using an aluminum film sample; October - investigate the non-thermal melting structure dynamics in a film with a laser heater.

The Development of a Laser Based Photoemission Facility for Studies of Strongly Correlated Electron Systems

LDRD Project 08-039

P.D. Johnson

PURPOSE:

The objective of this research program is to establish a photoemission facility based on the use of a laser as a source. The use of such a source has two objectives. Firstly, it is widely believed that the use of the lower photon energies available from a laser based source will result in a more sensitive PES experiment. This has never really been confirmed and needs to be investigated. Secondly the laser source is a high rep rate 75Mhz source that represents an ideal source for investigating the properties of a new high resolution time of flight (TOF) electron spectrometer developed at BNL.

APPROACH:

A laser based source that produces UV radiation by frequency doubling and quadrupling will be commissioned in the new laser laboratory in building 480. A new time of flight electron spectrometer that has been designed at BNL will be constructed and commissioned. These two separate components will be brought together to establish the laser based PES facility.

TECHNICAL PROGRESS AND RESULTS:

The TOF electron spectrometer is in the final stages of assembly. Shown in figure 1. the design involves the coupling of a parabolic collection mirror to a "velocity filter" that employs oscillating electrostatic fields to select electrons of particular energies. All components of the mirror and filter have been coated with a conducting surface to equalize all work functions through the detector. New methods were developed for attaching a grid to a machined surface having the exact parabolic curvature. In fact the methods used to do this have subsequently been used for mounting samples in a UHV environment.

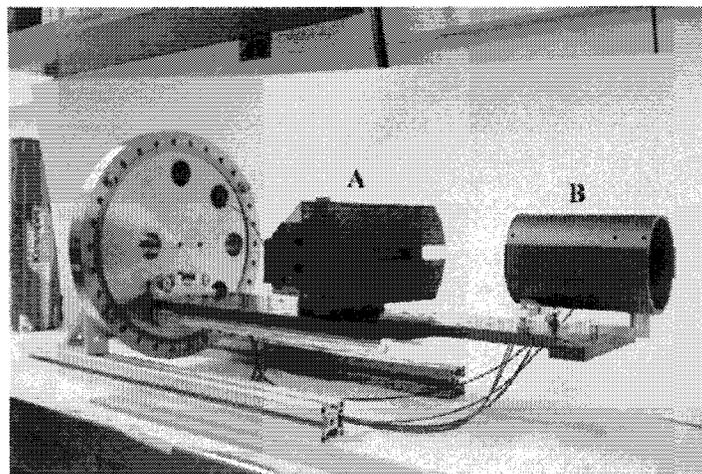


Fig. 1 *The assembled Time of Flight Spectrometer. The spectrometer couples an aberration corrected electrostatic parabolic mirror, A, to a velocity selecting filter, B.*

Preliminary work has also begun on developing the appropriate Labview based software to drive the spectrometer. The latter will be installed in a vacuum vessel that has been especially designed to minimize magnetic and electrostatic fields that might interfere with the low energy

electrons. The latter chamber shown in figure 2 has been designed constructed and tested for residual magnetic fields and vacuum tightness. The magnetic field was found to be less than 3 milligauss.

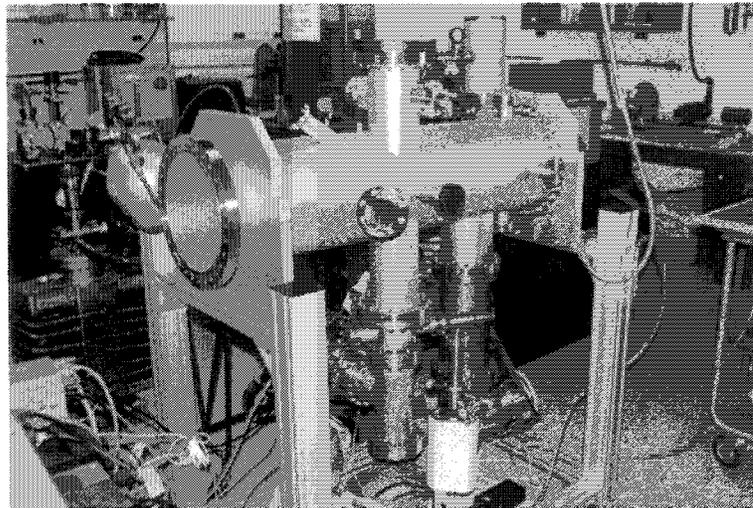


Figure 2. The vacuum vessel with an additional mu-metal liner that will be used to accommodate the time of flight spectrometer.

An 80 MHz Mira Ti:S laser pumped from an 18 watt diode pumped solid state Nd:YVO laser that can produce femto or picosecond pulsewidths, a synchrolock to slave it to the spectrometer and a UHV monochromator/spectrometer have all been installed in building 480. A second femtosecond Mira laser, with the same rep rate, as well as a stretcher/compressor and a regenerative amplifier are also installed in the same laser laboratory. These different systems may be configured to allow direct photoemission experiments via the use of frequency doubling and quadrupling or 2ppe pump-probe type experiments.

Theory of Electronic Excited States in Heterogeneous Nanosystems

LDRD Project 08-042

Mark S Hybertsen

PURPOSE:

Understanding and predicting the energy level alignments in heterogeneous nanosystems is both important and very challenging for theory and computation. Predictive theories of electronic excitation energies are well established, but they are severely limited in the scale of systems that can be treated with present day computational capabilities. I plan to explore physically motivated approximations that may result in a significant improvement in the efficiency of these calculations for nanosystems and to implement these improved methods exploiting large scale parallel computing. If successful, this research could enable excited state calculations for systems comparable in size to those treated with conventional Density Functional Theory, a significant technical breakthrough. For BNL and the CFN specifically, this project will nucleate a new computational electronic structure research effort, attract external users to the CFN, and enable partnerships with key external groups.

APPROACH:

Prediction and understanding of the excited electronic states of nanomaterials are frequently essential to explain and modify their function. Examples include electron transfer through a molecular bridge, the active electronic states in novel photocatalytic nanocrystals, and resonant energy transfer in light harvesting structures. Large scale applications of Density Functional Theory (DFT) based computations enable theoretical understanding of chemical bonding and other important properties in such systems. However, the orbital energies from DFT calculations do not accurately model electronic excitation energies. For example, they are empirically found to poorly approximate key quantities such as the band gap in semiconductors or the ionization potential of molecules, although overall trends may well be useful. So-called hybrid functionals (e.g. B3LYP) give more accurate bond energies and are now widely used in quantum chemistry. A recent modification of this approach for solids resulted in improved band gaps for semiconductors [1]. However, this approach still misses essential physical processes, particularly the image potential effect that plays a critical role in heterogeneous nanosystems. Predictive theories of electronic excitation energies are well established, but entail substantially more complex calculations. As a consequence, while ground state calculations are now done for systems of order 1000 atoms, excited state calculations are limited to systems of order 100 atoms.

In my recent research in collaboration with Neaton and Louie (Molecular Foundry, LBNL), the well-established, full GW approach was applied to benzene on graphite, an example of a molecule coupled to a metal electrode [2]. The GW approach includes the image potential effects and we demonstrated the strong influence that the environment has on the benzene excitation energies [2]. However, the GW approach is computationally very demanding. Our treatment of the benzene on graphite was among the largest systems that can be treated today, of order 100 atoms. Many applications to interesting nanosystems are presently out of reach. Analysis of the benzene calculations showed that the change in electron correlation energy on the molecule due to interaction with the surface was largely due to static polarization effects [2]. This result suggests to me that a static approximation in the GW framework can be developed that will be broadly applicable to heterogeneous nanosystems. I envision an approximate treatment based on the GW framework for electronic excitation energies that can be applied

broadly. In addition to the non-locality of exchange, it will account for polarization and screening explicitly. The latter is required to capture image potential effects. The feasibility and potential accuracy needs to be analyzed and the computational complexity must be explored.

I plan to investigate a new hierarchical analysis of the GW approach as a basis for a static approximation. This results in significant technical simplifications. The accuracy needs to be tested for prototype materials systems by direct comparison to complete GW calculations, e.g. for bulk materials like Si and for the interaction between small molecules to understand the applications to heterogeneous systems. Another critical issue concerns the necessary calculation of screening properties. A full calculation of the polarizability is equally as demanding as the evaluation of the full GW self energy. Research directed to identifying and implementing an efficient model screening approach will be undertaken. Candidate approaches include a model from my earlier research [3] and coarser grained solvation approaches [4]. In the first step, we require a model that adequately captures the local fields that most influence the electronic states of physical interest. Longer term, we seek a model that can be smoothly coarse grained to allow treatment of longer range environmental effects in heterogeneous nanosystems.

I plan to focus test calculations on a class of materials that are both technically challenging and more broadly significant for photocatalysis: N substituted titanates. The key physical question is the search for reduced band-gap oxynitrides that will both make better use of the solar spectrum and have frontier energy levels that properly align to the key electrochemical potentials for water splitting. The GW method will give a quantitative approach to this energy level alignment problem. This application will enable future collaboration with CFN users interested in photocatalysis, specifically Peter Khalifah (SBU and BNL Chemistry).

TECHNICAL PROGRESS AND RESULTS:

I have hired a new Research Associate, Wei Kang, who started in July, 2008. In his first three months of research, he has quickly learned the basic elements of the GW approach, ported a local version of the necessary GW codes to the CFN cluster, developed an interface to a widely used DFT package (PWSCF) and started GW calculations for TiO₂ and model titanates. He has also started testing new approximate treatments of the self energy operator in the GW framework.

March, 2009: complete GW based analysis of energy levels in a prototype N substituted titanate.

March, 2009: complete analysis of new static approximation to the GW self energy operator.

September, 2009: connect research on titanates to Khalifah experiments and support calculations performed under his CFN user agreement.

September, 2009: develop efficient model approaches to polarizability.

July, 2010: more complete testing of new approaches & implementation of parallel codes.

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Nanofabrication Methods Using Solution-Phase Nanomaterials

LDRD Project 08-043

C. T. Black

PURPOSE:

Our project will first create and implement a unique new fabrication method for uniform large-area assembly of solution-phase nanomaterials. The objectives are to implement this technique first for studying photogenerated charge transport in semiconductor nanocrystals. We will pursue new photovoltaic device designs incorporating multiple types of semiconductor nanocrystals to create heterojunction solar cells, and understand changes in their performance in response to systematic variation of nanometer-scale template dimensions.

APPROACH:

Solution-phase chemical synthesis has long provided a successful method for creating a diverse assortment of nanomaterials in liquid solutions. Detailed understanding of chemical processing conditions has resulted in well-characterized recipes for precise control of nanomaterial shapes (e.g., nanocrystals, nanowires, nanotubes), sizes, and material compositions. Although this high degree of tunability brings associated control of electronic and optical properties, there are relatively few examples of solid-state materials and devices incorporating solution-phase nanomaterials. The main barriers to application stem from a dearth of precise methods for nanomaterial deposition from solutions into large-area solid-state structures. This challenge is common to many areas of nanotechnology – the need for accurately positioning *nanometer-scale* elements across *centimeter-scale* areas.

Our project will create a wide-ranging fabrication technique for building complex solid-state electronic structures from solution-phase nanomaterials. The project will proceed along three specific directions focused first on refining this innovative fabrication method; demonstrating its utility through device fabrication for study of photogenerated charge transport in semiconductor nanocrystals; and finally applying the technique toward heterojunction solar cell devices

Expected project collaborators include Dr. Chang-Yong Nam (CFN) and Professor Chris Murray (UPenn).

TECHNICAL PROGRESS AND RESULTS:

The project is just beginning in December 2009 due to an extended search for a postdoctoral researcher suitably qualified to lead the effort. Dr. Jonathan Allen, Ph.D., from Northwestern University will join the project on December 8, 2009. Jon brings significant relevant experience to the project, including: (1) Deep knowledge of minority carrier transport in one-dimensional semiconductor wire devices. (2) Thin-film device nanofabrication, characterization by electron microscopy methods, and electronic device characterization. (3) Experience with laboratory automation using LabView software.

With Jon starting work at year-end 2008, I expect rapid progress with regard to project goals in 2009-2010.

2009 Milestones:

- Develop aluminum anodization process for forming self-assembled porous alumina templates, including control of pore size, separation, and template height
- Automate anodization process using LabView control of robotic dip-coater
- Develop target photovoltaic device concepts based on solution processing of nanomaterials (e.g, nanocrystals) and porous templates
- First photovoltaic device implementation; compare performance of templated and untemplated devices

2010 Milestones:

- Understand device performance changes in response to varying template dimensions
- Second, more complex photovoltaic device implementation incorporating multi-component nanocrystals

Identification of Organic Aerosols and their Effects on Radiative Forcing

LDRD Project 08-051

Yin-Nan Lee

PURPOSE:

The purpose of this LDRD project is to develop a technique for the determination of molecular weights of a class of organic constituents resembling humic acid present in ambient aerosol particles. The information gained with this new organic aerosol characterization technique will help better understand the formation, distribution, and optical and radiative properties of atmospheric aerosol particles and their effects on Earth radiation budget. This research is important to the DOE Climate Research component as directed by the Atmospheric Science Program (ASP). Support for deploying this technique in future ASP field measurement programs is expected.

APPROACH:

Quantifying aerosol radiative effects requires knowledge of spatial and temporal distributions of aerosols (size and number concentration) and their chemical composition that determines their optical and cloud condensation nuclei properties. At present, these aerosol properties cannot be reliably predicted, resulting in an IPCC assessment that aerosol forcing estimates are the most uncertain among that of the major forcing agents. A key limitation to achieving this predictive ability is a poor understanding of the role organic compounds play in aerosol formation, evolution, and properties. Effort to identify aerosol organic constituents regarding their concentrations and molecular structures represents an important step to improve this understanding.

Traditionally, aerosol organics were analyzed using the gas chromatography-mass spectrometry (GC-MS) technique applied to samples collected on filters. Although a large number of non-polar organic species have been identified, these compounds cover typically less than 20% of the total organic mass because the GC-MS technique is suitable only for volatile and thermally stable species. To identify the less volatile organics which invariably contain polar functionalities, the liquid chromatography-mass spectrometry technique has been used in recent years. These studies however show that an appreciable fraction of the soluble aerosol organics is a complex mixture of compounds of high molecular weight (MW) containing polymeric phenolic and carboxylic moieties. Because of their resemblance to humic acid in molecular properties, these compounds are referred to as humic like substance (HULIS). The sources and formation mechanisms of HULIS are unknown and must be identified.

In this LDRD project, we will determine the molecular weights and concentrations of HULIS, and to investigate their possible sources based on air mass history inferred from concomitant measurements, including CO, O₃, and air back trajectories. Specifically, the MW of HULIS will be characterized using a high performance liquid chromatography-electrospray ionization-mass spectrometry (HPLC-ESI-MS) technique which allows molecular ions to be detected. Several unique approaches we will take to aid this research are described below.

(1) Aerosol samples will be collected using a particle-into-liquid sampler (PILS) technique instead of the conventional filter based technique. Since PILS collects aerosol particles directly as aqueous samples, possible contamination associated with the filter technique, e.g., handling of filters during preparation and extraction and extended exposure of samples to atmospheric chemicals, e.g., oxidants, can be avoided.

(2) The HPLC separation will use both a reversed phase column and a size exclusion column that are calibrated/characterized using known MW compounds to provide additional MW information of the HULIS.

(3) As the success of ESI-MS depends on efficient ionization of the analytes, we need to select the appropriate ionization techniques (e.g., acidification, deprotonation, and ion adduct technique) and conditions (e.g., solvent composition and pH) for a specific class of analytes. To assess and optimize the ESI-MS detection, an evaporative light scattering detector (ELSD) will be used in parallel to provide mass concentration of the eluted analyte for comparison. The ELSD is a highly sensitive mass-based detector whose principle involves nebulizing and drying the eluate from the column and detecting the resulting aerosol particles comprising the analyte using the light scattering technique.

(4) We will make simultaneous aerosol chemical composition determination during the PILS sampling using an Aerodyne Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS) to provide concentrations of inorganic species and the total organics. Ancillary measurements needed to gain insights into the sources (e.g., combustion, biogenic) of HULIS, such as CO and O₃, will also be made during the aerosol sampling period.

TECHNICAL PROGRESS AND RESULTS:

An ESI-MS (Finnigan LCQ Advantage, Thermo Scientific) was set up and calibrated using several known compounds to test the efficiencies of different ionization techniques. The mass accuracy of the ESI-MS was tested using diethylene triamine pentaacetic acid (DTPA) against both the parent ion and daughter ions produced using a MS-MS technique whereby a selected parent ion is fragmented using the collision-induced ionization technique. Humic acid (HA) and fulvic acid (FA) obtained from International Humic Substance Society were tested without column separation. The mass/charge distribution patterns of HA and FA showed an average MW of ~1500 D and 900 D, respectively, assuming the ions are singly-charged similar to DTPA.

An ELSD (Agilent Technologies, Model 1200) was purchased. With a limit of detection of 1 ng, the ELSD provides the high sensitivity required for atmospheric constituents present in minute quantities. This detector was incorporated into the Thermo LCQ HPLC system in parallel to the ESI-MS. Preliminary tests using caffeine showed the limit of detection is near the specified value.

We expect to accomplish in the second budgeted year the following:

1. All instruments, ESI-MS, HPLC, ELSD, PILS, and ToF-AMS, will be on line by February 2009.
2. Atmospheric samples will be collected and analyzed during February, May, and August of 2009 to cover a seasonal dependence of HULIS.
3. Final report on the progress of this LDRD will be made in December, 2009.

As a footnote, the first year beginning Jan 2008 was devoted to the acquisition and set up of the key instruments. Resurrecting a dated ESI-MS (Finnigan LCQ Classic) originally planned was started but then delayed and eventually abandoned due to personnel changes. Dr. Linda Bowerman originally budgeted for this program left the Atmospheric Sciences Division in March; she was replaced by Dr. Cleve Dodge of Environmental Research and Technology Division who allowed us the access to a functioning Thermo Finnigan ESI-MS instrument. Sampling of atmospheric aerosols slated for the end of the 2008 was postponed because the PILS and ToF-AMS were devoted to the 2008 VOCALS field program in Chile and are unavailable till January 2009.

Computational Climate Science

LDRD Project 08-060

Andrew Vogelmann

PURPOSE:

Assessments of the potential impacts of pollution on climate are hampered by an incomplete understanding of the atmospheric physical processes needed in climate models. Our objective is to assess and improve these physical processes via model simulations that will be run on the New York Blue (NYB) supercomputer by a team of researchers from BNL and the Institute for Terrestrial and Planetary Atmospheres at Stony Brook University (SBU). The follow-on implications of this research, in terms of new programs and BNL institutional strategy, are: (a) establish a climate science modeling institutional capability on NYB; (b) foster cross disciplinary collaborations within BNL and between BNL and SBU; (c) support the EENS Strategic Initiative in Climate Research; and (d) support the FY08 Laboratory Strategic Initiative in Computational Science by expanding the range of scientific applications that would run on NYB.

APPROACH:

Accurate simulation of convection is an ongoing challenge that effects climate model transports of water vapor, cloud, and aerosol. We endeavor to improve our understanding by using the tropics as a convection testbed to determine whether explicit convection treatments are needed in global climate models to accurately simulate convection and aerosol transport. Simulations are run on the NYB supercomputer with successively high resolutions, and will be validated using newly available satellite observations and observational techniques developed at BNL.

- NYB atmospheric simulations use the Weather Research and Forecasting (WRF) Model, and its chemistry module extension WRF/Chem. WRF is a next-generation mesoscale model designed for atmospheric research that is ported to NYB as part of this project.
- WRF simulations are evaluated using new cloud and aerosol observations that provide constraints and insights into the model behavior: (a) an artificial neural network (ANN) developed by BNL researchers that uses satellite data to characterize tropical cloud fields and their behavior; (b) new aerosol observations from the Calipso space-borne lidar that provides the first routine, global observations of aerosol vertical profiles and particle size.
- We target the most deficient physical processes by exploiting NYB computational power to perform ensemble runs to map the variances of the model solutions in a phase space that considers the uncertainties in the model parameters and boundary conditions, especially those associated with convection.

The team is an interdisciplinary group of computer scientists and researchers at BNL and SBU that capitalizes on existing expertise. BNL units involved include the Atmospheric Sciences Division (Vogelmann, Guo, Luke, Daum, Huang, Jensen, Johnson, Liu, McGraw, Troyan), the Scientific Information Systems Group (Wagener, Cialella, Behrens, Gregory), and the Computational Science Center (Davenport, Efstathiadis, Slatest, Cortijo, Lamberti). The primary SBU faculty involved in this effort are Drs. Zhang, Colle, Lin, Jiao, Khairoutdinov, and Chang.

The novelty of this work is in the modeling approach that requires NYB computational power, and the use of newly available satellite observations. The risks are: (a) this level of WRF modeling (long simulations at high resolution for a large domain) has not been attempted before and could trigger instabilities, and (b) the core observational and modeling capabilities exist at BNL and SBU, but they have not worked together before on such a comprehensive study.

TECHNICAL PROGRESS AND RESULTS:

1. Model and Software Installations: (a) ported WRF v3.0 to NYB, which required resolving multiple issues with running the preprocessing system on NYB; (b) installed or coordinated with the New York Center for Computational Sciences to install critical software utilities and graphics packages (NetCDF, PNetCDF, Qt, Tcl, NCAR Graphics, NCL, NCO, RIP4, Ncview); (c) developed a script to assist with the optimal execution of NYB jobs; and (d) conducted scaling studies to find that WRF runs at > 80% efficiency out to 8 racks. These studies involved the only full-machine scientific run on NYB.
2. In collaboration with a team of supercomputer scientists led by J. Michalakes (National Center for Atmospheric Research; NCAR), we set a U.S. parallelization record for an experimental version of WRF, where 15 of the NYB 18 racks (83% of the full machine) were used at 91% efficiency. This work was presented for one of four Gordon Bell Prize finalists at the Supercomputing '07 Conference, and an internal BNL press release was issued (http://www.bnl.gov/today/story.asp?ITEM_NO=498).
3. Established a collaboration with Dr. Courtney Schumacher (Texas A&M) to investigate whether our satellite ANN can be trained on scanning C-Pol data to distinguish among precipitation regimes. The preliminary results have been surprisingly encouraging and, if successful, would enable a method for determining diabatic heating across the tropics for evaluation of tropical convection simulations.
4. Established a BNL-SBU climate science virtual institute to combine our complementary strengths in observational and process-oriented studies (BNL) with climate modeling and numerical weather prediction (SBU) to develop new approaches in modeling & data integration to improve climate-related processes in weather and climate. Activities included: (a) held 2 joint BNL-SBU climate science workshops, where each was attended by about 25 researchers and VIPs from SBU, BNL and IBM; (b) established a Climate Science Wiki for public visibility and private communications on project coordination; (c) held joint tutorial sessions on how to run WRF, the NCAR Community Climate System Model, and the NCAR Data Assimilation Research Testbed; and (d) team members attended a joint BNL-SBU-NCAR-PNNL meeting held at NCAR for developing regional climate model capabilities.
5. Overall, activities this fiscal year have resulted in: (a) 2 submitted publications; (b) 6 Meetings, proceedings and abstracts; (c) 1 project review; and (d) 3 proposals for follow-on funding (for details, see the LDRD Collections Form).

MILESTONES

FY09: (a) Port WRF/Chem to NYB and conduct scaling tests; (b) obtain WRF boundary condition data for conducting tropical simulations; (c) conduct tropical ensemble simulations on NYB for one-month periods using different model resolutions; (d) develop a software module

that relates WRF cloud simulations to satellite observed outgoing longwave radiation (OLR); (e) complete development work on the ANN to determine precipitation regimes from satellite data.

FY10: (a) Submit publication on ANN precipitation regimes; (b) use the BNL cloud tracking and ANN algorithms on the WRF OLR fields to obtain the model statistics of cloud movements; (c) Assess the modeled statistics to those observed to determine model deficiencies in the convective simulations.

A Novel Spintronic Room-Temperature High Purity Germanium X- and Gamma-Ray Spectrometer

LDRD Project 08-062

Giuseppe Camarda and Aleksey Bolotnikov

PURPOSE:

This proposal addresses the serious need for high-resolution, room-temperature X-ray and gamma radiation spectrometers for nuclear non-proliferation, homeland security, and synchrotron applications. High-Purity Germanium (HPGe) is the world's preeminent radiation detector material, because of its unique combination of material perfection, excellent charge transport properties and unsurpassed spectroscopic performance. However, the room-temperature band-gap of germanium is only 0.74 eV, and thermal charge generation must be suppressed by cooling the material to near liquid nitrogen temperatures, otherwise, the noise in the device is too large to provide spectral information. The necessity of cooling HPGe radiation detectors is both costly and cumbersome, and it has limited the utility of these devices. The energy resolution of HPGe detectors operated at liquid nitrogen temperatures is below 0.5%, and there has been an enormous push to develop a room-temperature detector that can provide the same energy resolution. The search has proven difficult and has recently focused on wide band-gap compound semiconductors, such as CZT, CdTe and HgI₂. These detectors currently can provide a room-temperature energy resolution near 1-2% @ 662keV, but the material imperfections have limited the size and corresponding detection efficiency of these devices. Therefore, none of the existing room-temperature radiation detectors have provided the combination of cost and performance necessary for security and synchrotron uses. A new spintronic high-purity germanium gamma-ray detector concept is proposed. Spintronic devices are based on the manipulation of an electron's spin state in addition to its charge, and have the potential to result in order-of-magnitude scale improvements in the performance of various semiconductor devices. In this project we will investigate the feasibility of applying spintronic principles to the production of a gamma-ray spectrometer based on HPGe that operates at elevated temperature.

APPROACH:

Semiconductor spin electronic devices offer great promise as a revolutionary technology for detecting radiation. Despite significant effort and investment worldwide, commercial semiconductor spintronic devices have not been realized. This fact highlights the challenge inherent in any semiconductor spintronics project.

We propose to undertake initial steps towards constructing a spintronic gamma-ray detector using semiconductor material, such as High-Purity Germanium (HPGe) and Si.

We will deposit high-quality epitaxial ferromagnetic contacts on HPGe (and Si) and test for unambiguous spin-transport signatures via nonlocal magnetoresistance measurements.

We anticipate realizing a measurable enhancement in resistance in the device structure compared to a non-magnetic-contacts reference one.

The success of our work under this project will afford proof-of-principle for the world's first spintronic gamma-ray spectrometer. Our development of the proposed spintronic detector could revolutionize the field of gamma-radiation detection and provide a room-temperature energy resolution far surpassing any existing instrument.

TECHNICAL PROGRESS AND RESULTS:

For FY08 (Jan08 – Oct08), the team has acquired the raw material needed for the structure fabrication. The germanium crystal was sliced and polished into wafers of 0.5mm, 1mm and 1.5mm thickness (Fig. 1).

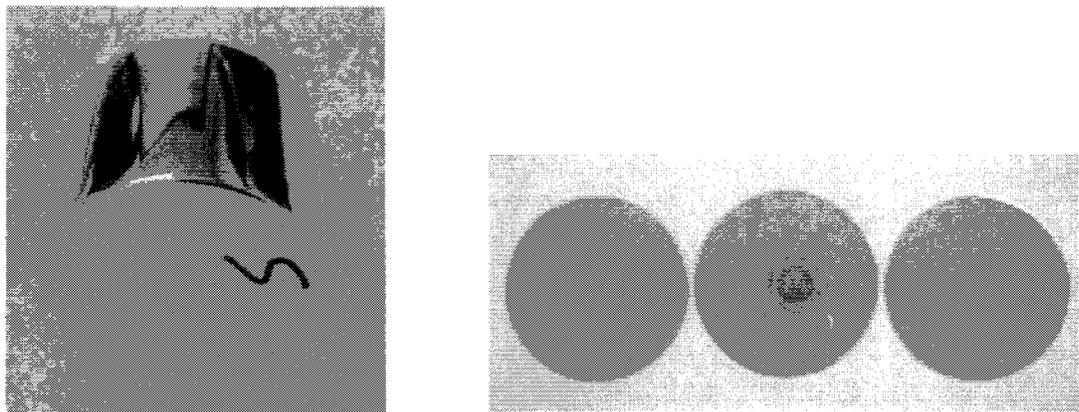


Fig. 1 Photo of the germanium ingot and the Ge wafers.

Surface preparation/cleaning procedures involving a combination of chemical rinsing, mechanical polishing and plasma cleaning were developed.

We have begun investigating several possibilities for the deposition of ferromagnetic contacts on Ge, which is a key step in the spintronic detector design.

For FY09, we will design and fabricate the photo-masks to fabricate a device structure with Ge to observe spin-transport. We anticipate realizing a measurable enhancement in resistance in the device structure compared to a non-magnetic-contacts reference one.

Tracer Development- Improving PET and MR Imaging

LDRD Project 08-080

Joanna S. Fowler and Fritz Henn

PURPOSE:

The purpose of this proposal is to develop new scientific tools for molecular imaging. This includes developing new synthetic methods for PET radiotracers as well as new targeting and quantification methods and their translation to animals and humans. This program covers both small molecules and nanoparticles. A special focus is placed on fundamental chemistry with carbon-11 to lay the groundwork for the synthesis of a variety of carbon-11 labeled radiotracers. With recent the shift in program mission from nuclear medicine to energy and environment, we also increased our efforts on the development of radiotracer and radioanalytical methodology for studies of plant metabolism. Two molecular targets are aromatase, an enzyme involved in estrogen (and phytoestrogen) synthesis and histone deacetylase (HDAC), an enzyme involved in epigenetic processes. The development of new scientific tools for plant science is undertaken with a view of adding new knowledge and attracting outstanding collaborators in plant science to facilitate alignment with DOE-BER's mission. Innovations in radiotracer chemistry will also be transferable to NIH grants and CRADA projects with pharmaceutical companies.

APPROACH:

Innovation in radiotracer chemistry has been the main driver in advancing the molecular imaging and nuclear medicine fields. Building on Brookhaven's longstanding history in radiotracer development for neuroscience and responding to the program reorientation to energy and environmental applications, we set out to (1) develop new radiotracer synthetic methods which could be applied to a broad array of molecular structures thereby opening up the ability to imaging new biological targets across species; (2) to develop labeled compounds with specificity for aromatase and HDAC; (3) to develop kinetic analysis methods for quantification of these targets; (4) to develop a radiotracer toolkit and radioanalytical methods and imaging for plants; (5) to develop labeled nanoparticles for nanotoxicology studies; (6) to establish new collaborations with scientists in energy and environment applications; (7) to set up current Good Manufacturing Practice (cGMP) for radiotracer preparation for humans studies (required for some pharmaceutical company CRADA's); (8) to train scientists in molecular imaging, thereby responding to the critical shortage of chemists in the nuclear medicine field as documented in the 2007 National Academy of Sciences report (*Advancing Nuclear Medicine through Innovation*).

TECHNICAL PROGRESS AND RESULTS:

We have made the following progress:

- We developed a new rapid synthesis of [^{11}C]formaldehyde from [^{11}C]methyl iodide making this useful precursor readily available for the first time.
- We developed a method to carbon-11 label salvinorin A, a kappa opioid receptor specific molecules and carried out the first PET studies of its kinetics in primates demonstrating that the rapid entry and clearance of this molecule from the brain parallels its intense short term behavioral effects in humans.
- We have studied the brain pharmacokinetics and pharmacodynamics of the stimulant drugs methamphetamine and modafinil demonstrating relationships between brain kinetics and

behavioral effects and showing shedding light on the molecular mechanism of action of the atypical stimulant modafinil.

- We developed a method to synthesize and purify [¹¹C]vorozole for measurement of aromatase activity and we validated it in animals and prepared a human use application. We have also proposed the use of this radiotracer for phytoestrogen metabolism in plants.
- We developed an improved synthesis for the HDAC tracer [¹⁸F]FAHA and developed a kinetic model for quantification.
- We have instituted a method to analyze for epigenetic patterns (DNA methylation) in DNA samples and we are applying it to DNA samples from human subjects in whom we also have genotyping and brain chemistry measures.
- We developed a radiotracer toolkit and plant metabolism laboratory for in vivo study of plant metabolism and the factors governing the conversion of CO₂ to energy rich molecules.
- We have developed a rapid synthesis of [¹¹C]nanoparticles and used this as the basis for a proposal on nanotoxicology to Battelle.
- We have initiated a project to make radioiron labeled nanoparticles which can be decorated with targeting molecules (example, antibodies) for dual modality imaging (PET and MRI).
- We implemented cGMP and completed two CRADA projects with pharmaceutical companies. This contributed significantly to funding our infrastructure for human studies.
- We have completed the first placebo controlled trials of GVG in cocaine abusers. This body of work received a K award from NIH providing partial salary support for the PI.
- We have initiated collaborations to transition into energy and environment applications. One of these is with Dr. Patricia Sobecky of the University of Georgia who is interested in using radiotracers to track uranium particle migration in soils. Another is Dr. David Jackson, Cold Spring Harbor Laboratory who is interested in using radioanalytical techniques to monitor sugar signaling in plants.
- This year we graduated a PhD student in chemistry (SBU) specifically in radiotracer chemistry. We also hosted 4 graduate students from the University of Mainz who did a one-semester project in radiotracer chemistry. This is a continuation of a program that has been in effect since 2002 and which has hosted 18 student who came to BNL to take the Nuclear Chemistry Summer School and to do a research project in radiotracer chemistry. In keeping with the program reorientation to energy and environment, one of these students did a plant project using radiotracers to measure the rate of conversion of sugar to cellulose using ¹⁸FDG. We also continue to direct the Nuclear Chemistry Summer School (R. A. Ferrieri).

In summary, we have begun the process of integrating plant science into our radiotracer R&D and instrumentation development program in response to the change in mission. The radiotracer development work in nanoparticles and in epigenetics and estrogen metabolism is well aligned

with the new mission. We will also continue developing radiotracer synthetic methods and integrate this with instrumentation development for plants. We have the following milestones:

- Milestone 1: In the coming year we will prepare a new Scientific Focus Area (SFA) proposal combining our FWP's into one SFA which will have an energy/environment focus.
- Milestone 2: As part of the SFA, we will be applying for funding for a post doctoral fellow from the laboratory of Patricia Sobecky (uranium migration in soils) and from the laboratory of David Jackson (plant genetics) to build up the energy and environment area.
- Milestone 3: Through the implementation of cGMP, we have positioned ourselves to take on more pharmaceutical company projects and NIH projects to maintain and support our clinical neuroscience program. We have initiated contacts with Wyeth Pharmaceuticals and with Bristol Myers Squibb Pharmaceuticals to explore new CRADA projects at Brookhaven.
- Milestone 4: We plan to apply for an NIH training grant to support the training of graduate students in imaging sciences.

Development of MR Research at BNL

LDRD Project 08-081

Fritz Henn

PURPOSE:

The goal of the program is to make significant contributions to human MR imaging. This has involved both the application of new paradigms to fMR studies, the development of MRS methods and the use of trans-cranial magnetic stimulation to stimulate specific brain areas. The major effort in the past year has focused on the use of new paradigms for fMRI and the study of various mental states as well as the development of reliable trans-cranial magnetic stimulation paradigms and an analysis of which structures can be reliably stimulated with trans-cranial magnetic stimulation. The technology developed including multi-modal imaging using PET, MR and EEG to study the same paradigm has led to a detailed understanding of brain activation in addicted states compared to non addicted states. This has led to the development of a joint MR-PET scanner which has become a priority for the instrumentation group in PET..

APPROACH:

This project has two distinct threads one between Dr. Rita Goldstein and Dr. Tomasi is aimed at developing paradigms to help understand the differences in cerebral processing between addicted brains and non-addicted brains. This work involves multi-modal imaging using paradigms to probe cerebral processing, such as pictures of drug related paraphernalia which illicit craving in addicts and no special response in non-addicted individuals. This allows an analysis of the pathways which underlie craving and a way to probe methods to reduce craving. This also involves looking at the dopamine activity in these states using PET, as well as the changes in EEG responses under these conditions. Since the time scale and spatial resolution of these methods is very different combining them allows a much deeper understanding of brain mechanisms. Part of the effort of this program is to integrate the information from the three modalities using computational tools.

The second thread of this project is the collaboration between Dr. Tomasi and Dr. Caparelli is aimed at developing methods to stimulate specific brain regions using trans-cranial magnetic stimulation (TMS) in the MR machine and look at the circuit activated via activation of a specific region of the brain. This would be a major technical breakthrough for areas as diverse as cognitive psychology and neurosurgery. The use of TMS on the occipital cortex has resulted in stimulation of the visual cortex in initial experiments.

We also are continuing to develop sequences for MRS of glutamate and GABA which we are attempting to activate through specific activation of specialized brain pathways.

To date no group has been able to look at time dependant changes in glutamate or GABA activity as a function of brain activation and this is our goal.

TECHNICAL PROGRESS AND RESULTS:

The development of paradigms to measure salience resulted in 7 major publications in the last year and has led to a better understanding of the effect of addiction on attention and cognition. The methodology to put together data from various modalities has led to collaboration with computational science at Stony Brook. The same general approach has been developed with studies of aggression, also involving genetic and epigenetic influences on aggression.

Milestone: A further grant in the area of aggression using MR imaging is anticipated in the coming year.

The area of TMS stimulation awaits further development of TMS coils to increase the depth of penetration to allow stimulation of areas related to mood and anxiety. Coil design is moving forward and this project should result in a viable coil for deep brain stimulation.

Milestone: The creation of a TMS coil with the ability to stimulate structures under the cortex.

The area of MRS should lead to a study looking at the role of neurogenesis in depression and perhaps the ability to follow changes in GABA and glutamate in the brain as a function of regional activation.

Milestone: An NIH funded MRS project aimed at determining the role of neurogenesis in depression.

Biofuels and Nanotech for Improvement of Oil Heat Combustion Systems

LDRD Project 08-082

Thomas A. Butcher and Miriam Rafailovich

PURPOSE:

This work is focused on two specific aspects of biofuel end use: polymers for corrosion resistant condensing heat exchangers and fuel atomization.

High efficiency in end use applications is achieved through recovering latent heat from water vapor in the products of combustion. The condensate produced is acidic and heat exchanger metal surfaces are subject to high corrosion rates. In this project we are developing new polymer nano-composites for this application which are corrosion resistant, flame retardant and have high thermal conductivity. The second part of this project involves understanding the impact of biodiesel addition to fuel mixtures on the breakup process of fuel jets from atomizers. This basic study will lead to improved understanding of the impact that biofuels may have on flame development in combustion systems and, in turn, air pollutant emissions.

APPROACH:

The polymer composites are produced via a new system where nanoclays are used to form in-situ grafts that promote compatibilization, while at the same time providing the desired material properties. The materials are being produced at Stony Brook University and analyzed using the Scanning Transmission X-ray Microscope (STXM) at the Advanced Light Source in Berkeley. Corrosion resistance studies will be performed at Stony Brook where trace materials analysis will be performed. The new composites will then be tested on different designs of condensing heat exchanger units in an actual biofuel flue gas environment at BNL.

For spray formation studies, the project has planned to use the ultra fast imaging beam line at Argonne National Laboratory in order to visualize the combustion process of different types of fuels, including mixtures of biodiesel and different types of oils. The dynamics of injection as a function of the fuel viscosity, mixing of the fuels, and any surfactants will be studied in order to enable improved modeling of combustion processes and understanding of the fundamental mechanism through which biodiesel fuels produce increased NO_x emissions in many applications.

Project collaborators include: Jin Wang, Argonne National Laboratory; Harald Ade, Advanced Light Source, Berkeley, California; and Takashi Kashiwagi, NIST.

TECHNICAL PROGRESS AND RESULTS:

The start date for this project was July 15, 2008 and the end date is Sept. 30, 2009. The key focus to date has been on the production of clay nanocomposite polymers and evaluation of flame inhibition. We showed a synergy from the combination of modified organoclays with halogen flame retardant (FR) additives can render polymer blends self-extinguishing. Primarily, we investigated the fact that small amounts of the clays can lead to a large reduction of heat release rate (HRR) and mass release rate (MRR) in PS/PMMA polymer blends due to a formation of networks composed of the clay platelets, which made themselves nanotubes during combustion. In order to confirm this unique behavior of the clays, using transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), and Scanning Electron Microscopy

(SEM) degree of intercalated and exfoliated clays is confirmed at different high temperatures. In addition, the amount of the Br particles left after combustion was measured using energy dispersive X-ray spectroscopy (EDXS). Furthermore, Extended X-Ray Fine Absorption Structure (EXFAS) was used in order to verify a potential possibility of changing the chemical structure of the Br particle in the gas phase. We applied the synergy to a different polymer system, PC/SAN24, to confirm the effect on HRR and MLR. Even though the clays were compatibilized in PC/SAN24 polymer blend, the large reductions in HRR and MRR were not observed due to hindrance of the clays to chain scissions of PC, which leads to char formation. Therefore we believe that the synergy is able to occur when only non-cross linking polymers exist in a system. Moreover, the networks can make polymer blends self-extinguished because of its high thermal conductivity.

At BNL a test arrangement has been built for exposure of polymer samples to flue gas from biodiesel combustion under condensing conditions. Test have started with metal alloy heat exchanger samples to provide a baseline. Stony Brook will prepare several polymer composite samples to put into this test arrangement to evaluate durability when exposed to condensate from 100% biodiesel firing.

A proposal for the planned work at Argonne has been prepared and submitted but not accepted. This proposal is being revised and will be resubmitted.

The following paper has been submitted and accepted for publication: Pack, S., Kashiwagi, T., Koo, J., Sokolov, J.C., Koga, T., Weil, E., and Rafailovich, M., Self-extinguished polymer blends by introducing organoclays, *Polymer Degradation and Stability*, 2009.

Solar Water Splitting: Quantum Theory of Photocatalytic Processes at the Water/Semiconductor Interface

LDRD Project 08-083

P. B. Allen and M.-V. Fernandez-Serra

PURPOSE:

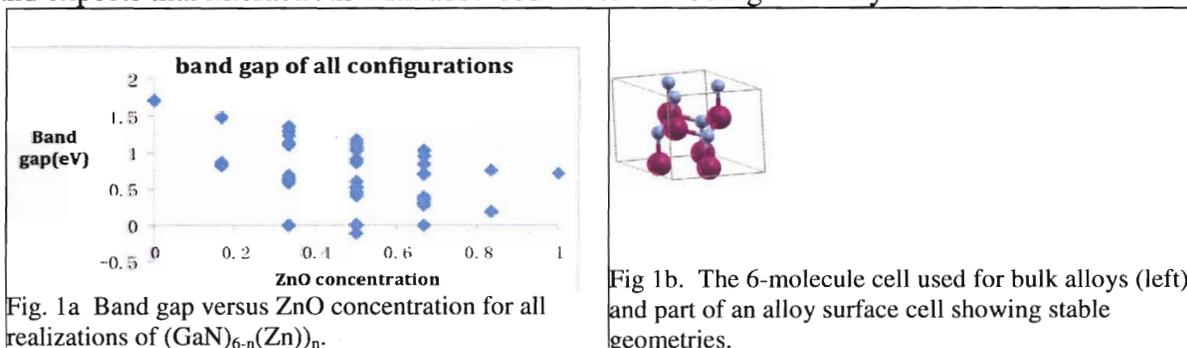
The aim of this project is to use microscopic theory of electronic structure to study the interface between a photo-active semiconductor that absorbs sun light, and water. At the interface, the reaction $2h^+ + H_2O \rightarrow 2H^+ + O$ is catalyzed, where h^+ is a photo-hole from the semiconductor and O is unknown oxygen intermediates that eventually react to form dissolved O_2 gas. The dissolved gas accumulates, aggregates, and leaves the solution. The free dissolved H^+ ions are available for further electrochemistry, such as $2e^- + 2H^+ \rightarrow H_2$, where e^- is the photo-electron. Thus is produced artificial (as opposed to biogenic) "solar fuel" in the form of hydrogen gas.

APPROACH:

This problem is being addressed by computational modeling on the BlueGene/L computer "NY Blue." We have participated in implementation on this computer of several software packages for electronic structure calculation. The work has mainly been done by two Stony Brook graduate students who are supported on this LDRD: Li Li (supervised by P. B. Allen) and Jue Wang (supervised by M.-V. Fernandez-Serra.) Their work is integrated with the Stony Brook/BNL working collaboration called SWaSSiT (the Solar Water Splitting Simulation Team). Both students are in their first year of research. A third and more senior Stony Brook student, Xiao Shen, works closely with this group on some related projects, funded by a DOE grant to P. B. Allen. His expertise has enabled the younger students to start up quickly. The group meets once a month at BNL and once a month at Stony Brook, to review progress, review the literature, and guide the work of the students.

TECHNICAL PROGRESS AND RESULTS:

Li Li has calculated the semiconductor alloy $(GaN)_{1-x}(ZnO)_x$, using theory to predict its bulk crystal structure and short-range alloy order. He has computed energies of many alloy geometries (Fig. 1b). He finds band gaps "bowing" below the linear extrapolation of the GaN and ZnO bulk band gaps (Fig. 1a). He finds a slightly positive formation energy for an ordered 50/50 alloy GaZnNO. He finds consistent results using LDA and GGA procedures. Mr. Li is also examining alloy surface structures. Northrup found that under oxygen atmosphere, it is favorable for a few oxygens to replace nitrogens on the (10-10) GaN surface. Li confirms this and expects that interactions with adsorbed water will be significantly altered.



Jue Wang has worked on optimizing pseudopotentials and atomic basis sets used in the DFT-based linear scaling program SIESTA, for the GaN/water system. This worked has allowed him to perform *ab initio* molecular dynamics simulations (AIMD) at 330K of a thick liquid water film at the same (10-10) non polar surface of GaN that Xiao Shen studied with just one monolayer of water and $T=0$. Much larger unit cells are used, to accommodate enough water molecules to model the liquid. Long molecular dynamic simulations are needed to sample the liquid energy landscape. He has already gotten more than 2 ps of sampling statistics, and, as seen in Fig. 2, most of the molecules that reach the surface do indeed spontaneously dissociate and stay at the surface, just as in the $T=0$ monolayer calculation.

Characterizing structural properties near a solid-liquid interface is not easy. Key questions are the following. (a) How rapidly does structure near the surface rearrange? How much is this inhibited relative to bulk water? (b) What are the electronic structure changes associated with these structural rearrangements? Computational sampling of solvent configurations at and beyond the surface is hostage to system size and to the time step of the molecular dynamics simulations. For water AIMD, a time step of 0.5 fs is used to integrate the equations of motion. Our systems contain up to 90 water molecules and 100 atoms of semiconductor. With these sizes, we obtain ~10 ps of trajectory after several weeks of calculations on NY Blue .

