FWP Title: RADIATION DAMAGE EFFECTS IN CERAMICS AND NON-METALS **Los Alamos National Laboratory**
FWP Number: LANLE409 **B&R Code: KC020102**

Program Abstract:
The goal of this program is to understand radiation damage effects in ceramics exposed to energetic particles. Our ultimate goal is to design new radiation-resistant ceramics. Radiation damage studies of ceramics involve: (1) prediction of microstructural evolution in ceramics exposed to radiation; and (2) identification of physical aspects of ceramics that are effective in promoting radiation resistance, particularly resistance to amorphization. We conduct irradiation tests on ceramics and composites, in order to evaluate their irradiation damage response. We perform computer simulations of damage evolution in ceramics to promote our understanding of radiation damage phenomena in these materials at the atomic scale. In particular, we apply accelerated molecular dynamics to reach experimentally-relevant time scales in our simulations and density functional theory to look at the role of disordering in materials. This allows us to assess the tendency of materials to disorder as well as the time scale for the recovery of order from the disordered state and is thus more directly comparable with experimental observations. We have examined the role of transmutation of radio-isotope species on the structural stability of the host lattice and have found unexpected crystalline phases. We expect radiation resistant ceramics to find application in existing fission reactors, in future fusion reactors or accelerator-based reactors, or as actinide-host ceramic fuel forms and waste forms.

Program Impact: This highly fundamental research program involves many laboratory and personnel resources that are unique to Los Alamos National Laboratory (LANL). For instance, there is a significant emphasis in this program on obtaining a fundamental understanding of radiation damage mechanisms in advanced nuclear reactor fuel forms. Our BES program benefits greatly in these research efforts from the fact that LANL is the *lead* laboratory in the U.S. for ceramic fuel R&D. BES researchers have the opportunity to work with the LANL ceramic fuel researchers who are sponsored by the DOE Office of Nuclear Energy, Fuel Cycle R&D program (and work in their facilities). This BES program also has a significant emphasis on obtaining a fundamental understanding of radiation damage effects in potential nuclear waste forms. Consequently, this BES program benefits from working collaboratively with several Fuel Cycle R&D efforts currently funded at LANL that relate to advanced separations and waste technologies. This BES program also benefits from a variety of special experimental and computational facilities that are unlikely to be available at most universities. These include: (1) Electron Microscopy Laboratory (EML); (2) Ion Beam Materials Laboratory (IBML); (3) Los Alamos Neutron Science Center (LANSCE); (4) Center for Integrated Nanotechnologies (CINT); (5) Weapons Nuclear Research (WNR) Center; (6) Isotope Production Facility (IPF); (7) High Performance Computing (HPC). Because of the complexity of the problems being investigated, it is crucial for this program to reside at the national laboratory in order to leverage existing expertise in areas that were not immediately apparent, including, for example, the EPR used in a recent publication with M. Blair to identify the charge and composition of an irradiated material. Finally, because of the unique environment within our BES program, experimentalists work hand-in-hand with theorists to develop a fundamental understanding of these materials, something that would not be possible on a single investigator grant.

FY 2009 Authorized Budget (New BA): $1,026,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:
Kurt Sickafus (Technical Staff Member, 0.40 FTE), Blas Uberuaga (Technical Staff Member, 0.30 FTE), Chao Jiang (Technical Staff Member, 0.3 FTE), Yongqiang Wang (Technical Staff Member, 0.25 FTE), Robert Dickerson (Technical Staff Member, 0.10 FTE), James Valdez (Technician, 0.50 FTE), Jonghan Won (Postdoctoral Research Asst., 0.50 FTE), Maulik Patel (Postdoctoral Research Asst., 0.50 FTE), Jian Zhang (Graduate Research Asst., 1.00 FTE), Yuhong Li (Visiting Scientist, 0.67 FTE).

Interactions: Amar, J. G. (University of Toledo); Blair, M. W. (Los Alamos National Laboratory); Bracht, H. (University of Münster); Chi, Z. (Renishaw Inc.); Chroneos, A. (University of Münster); Czerwinski, K. (University of Nevada – Las Vegas); Desai, T. G. (Advanced Cooling Technologies, Inc.); Deo, C. (Georgia Institute of Technology); Grimes, R. W. (Imperial College); Hartmann, T. (University of Nevada – Las Vegas); Hosemann, P. (Los Alamos National Laboratory); Huang, H. (University of Connecticut); Ichinomiya, T. (Hokkaido University); Ishimaru, M. (Osaka University); Jarvinen, G. D. (Los Alamos National Laboratory); Kinoshita, M. (Japan Atomic Energy Agency); Levy, M. R. (British Energy); Marks, N. A. (Curtin University of Technology); McClellan, K. J. (Los Alamos National Laboratory); Phillpot, S. R. (University of Florida); Shim, Y. (University of Toledo); Sinnott, S. B. (University of Florida), Smith, R. (Loughborough University); Srinivassan, S. G. (University of North Texas); Stanek, C. R. (Los Alamos National Laboratory); Usov, I. (Los Alamos National Laboratory); Voter, A. F. (Los Alamos National Laboratory); Watanabe, T. (Georgia Institute of Technology).

FWP Title: Deformation Physics of Ultrafine Scale Materials **Los Alamos National Laboratory**
FWP Number: LANLE410 **B&R Code: KC020102**

Program Abstract:

This program investigates the deformation mechanisms that enable unusually high strengths, approaching the theoretical limit for perfect crystals, in nanolayered metallic composites. The program involves a synergistic combination of atomistic simulations and experimental methods. The integrated approach consists of synthesis by physical vapor deposition; structure-property correlations by means of transmission electron microscopy and x-ray diffraction, including *in situ* testing; micro-tensile, micro-pillar compression and nanoindentation testing; and atomistic and dislocation dynamics simulations of deformation behavior.

Program Impact:

This program has discovered new regimes of plasticity in nanoscale composite materials and developed scientific models to understand the origins of unusually high flow strengths of nanoscale materials. Discoveries from this program significantly shaped the science basis for the nanomechanics thrust area in CINT, and a LANL-led EFRC: *Center for Materials at Irradiation and Mechanical Extremes*. The discovery of high radiation damage tolerance will significantly impact the design of structural materials for future nuclear reactors.

FY 2009 Authorized Budget (New BA): $814,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:

A. Misra (LANL, PI, 30%), R.G. Hoagland (LANL, 30%, retired April 2009), J.P. Hirth (LANL, Affiliate, 10%), N.A. Mara (LANL, TSM, 25%), P. Dickerson (LANL, TSM, 20%), D. Bhattacharyya (LANL, PD, 50%), J. Wang (LANL, PD 100% until August 2009; Staff 35% since September 2009), O. Anderoglu (LANL, GRA, 50%), N. Li (LANL, GRA, 50%), J. Kevin Baldwin (LANL, technologist, 50%), T.C. Germann (LANL, TSM, 30% starting FY'10), X.Y. Liu (LANL, affiliate, 50%).

Interactions:
H.M. Zbib & D. Bahr (Washington State University), P.M. Anderson (Ohio State University), I.M. Robertson (University of Illinois), T. Ungar (Eotvos University Budapest, Hungary), M. Uchic (AFRL), J. Almer (APS) and D.W. Brown (LANSCE, LANL), Nik Chawla (ASU), Mike Demkowicz (MIT), Xinghang Zhang (Texas A&M).

FWP Title: Multi-scale Study of the Role of Microstructure in the Deformation Behavior of Hexagonal Materials

Los Alamos National Laboratory
B&R Code: KC020102

FWP Number: LANLE7CT

Program Abstract:
We use an integrated experimental and theoretical approach to characterize dislocation and twin structures in HCP, their interactions, and the role that they play during plastic deformation. We go beyond the microscopic characterization of dislocations, grain boundaries and twins, and aim to quantify the role that they play on the overall mechanical response of polycrystals by linking the micro-macro scales. Such quest, which can only be answered through a basic and integrated study of such features, is the general scope of our program.
During FY09, focus one of this program has been to elucidate the basic mechanisms of twin nucleation and propagation in HCP, which are not well understood, although they play a primary role in plasticity. Focus two has been to incorporate the micro-scale knowledge into polycrystal constitutive laws, and benchmark those utilizing complex testing histories involving changes in strain path, temperature, and strain rate.

Program Impact:
Relating texture, anisotropy, and polycrystal-based constitutive descriptions of elasto-plastic behavior is relatively recent, and has changed the way in which the scientific community approaches constitutive modeling. In our opinion, this is the only viable approach to use for a general description of HCP materials. Results and methodologies developed within this program are being adopted by the Materials community, especially within the nowadays much increased research on Mg alloys for automotive applications. Two of those developments are our simulation codes VPSC (used for plastic deformation) and EPSC (used to interpret neutron diffraction measurements of internal strains). The latter is becoming known and used by the geologic community for interpreting high pressure in-situ experiments.

Also, techniques that we developed or are developing for microstructure characterization, are being adopted. Specifically: automated EBSD analysis of microstructural features, statistical analysis of the latter, and synchrotron X-ray measurements of stress states in grains and twins.

Our team at Los Alamos is regarded as leading the field in these issues. We predict that our specific focus on hexagonal aggregates - Zr, Mg, Be - will have a direct impact on basic material science, in Los Alamos research programs, and in energy related technologies, such as nuclear, automotive and aeronautics. We foresee that, once adapted, this methodology will impact the understanding of material systems where phase transformations play a role in evolving the anisotropy and determining the mechanical response, such as shape-memory alloys, TRIP steels and TWIP steels.

FY 2009 Authorized Budget (New BA): $981,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):
PI: C. Tomé (50%); **Technical Staff Members**: I. Beyerlein (40%), G Kaschner (25%), R. McCabe (25%), E. Cerreta (20%), B. Clausen (30%), D. Brown (15%). **Postdocs**: L. Capolungo (100%), J. Wang (40%); **Students**: J. Wolmershauser (100%, PhD).

Interactions: (limit to current interactions and collaborations)
Prof. J.P. Hirth (LANL consultant), Prof. S.R. Agnew (U. of Virginia), Prof. W. Horstemeyer (MS State U.), Prof. R.H. Wenk (UC Berkeley), Prof. S. Merkel (U. of Lille, France), Prof. I. Karaman (Texas A&M U.), Prof. L.Toth (U of Metz, France), .), Dr. S.I. Wright (TexSEM Labs)

FWP Title: Electronic Processes in Solid State Organic Electronic Materials **Laboratory Name:** LANL
FWP Number: LANLE412 **B&R Code:** KC020103

Program Abstract:
The field of organic electronic materials is in a state of rapid expansion. In addition to basic scientific interest, there are strong technology drivers for this field including: organic light emitting diodes for display applications, organic field effect transistors for large area electrical drive circuits, and organic optical detectors and solar cells. To date much of the work in this research area has employed an Edisonian approach. There is a very large material and device structure phase space in this field and we must move to a more predictive science based research approach. Organic electronic materials, also called organic semiconductors, are condensed phases of conjugated organic molecules. Because of their strong intermolecular interactions, the electronic properties of organic semiconductors are not the same as those of the isolated constituent organic molecules. A major theme of our research is to determine which features of the electronic properties of the isolated molecules are maintained and which are modified in the condensed phase. We are using an interdisciplinary research approach employing methods from condensed matter physics, quantum chemistry, and electrical engineering.

Program Impact:
Organic semiconductors are of great intrinsic scientific interest because of the rich spectrum of tunable ground and excited state properties that result from a competition between the strong coupling of charge, spin, and lattice degrees of freedom in these materials. Organic semiconductors have also become important for a broad class of technological applications because of their favorable processing, fabrication and performance properties. The overarching goal of this program is to develop an understanding of organic electronic materials and devices that spans scales from molecular structure through the physics of the novel devices that are fabricated from organic semiconductors. We are employing an integrated theory/fabrication/measurement approach to the study of organic semiconductors. Researchers with expertise in condensed matter physics theory and experiment, quantum chemistry, optical spectroscopy, and device physics and modeling are working together to obtain a fundamental scientific understanding of the important physical processes in organic semiconductors. We believe that this integrated approach is necessary to quantitatively understand the processes controlling the properties of these complex disordered materials and the devices fabricated from them.

In the study of organic semiconductors, it is valuable to make comparisons with inorganic semiconductors such as Si and GaAs. The study of electron spin based phenomena, spintronics, presents a good example. There has been a great deal of progress recently in the study of spintronics on inorganic semiconductors. Because of the very long spin lifetimes that result from the weak spin-orbit interaction in organic semiconductors, spintronic applications are expected to be particularly interesting in these materials. We have made extensive contributions to spintronics research in inorganic semiconductors and are making comparison studies of spintronics, from both microscopic materials and macroscopic device perspectives, in these two classes of materials. Our work is having a major impact on spintronics research in both organic and inorganic semiconductors and has led to collaborations at UCSB and U Minn. and serving on the advisory committee of a major international conference on organic spintronics (3rd Topical Meeting on Spins in Organic Semiconductors, Amsterdam, 2010; http://www.spinos.nl/). We have also used an approach based on comparison between organic and inorganic semiconductors to demonstrate high gain organic photodiodes and to establish methods to determine energy alignments at interfaces between organic and inorganic semiconductors.

FY 2009 Authorized Budget: $441,000

Program Personnel Supported in FY2009:
Ian Campbell, PI: 20%; Brian Crone, PI: 20%, Richard Martin, PI: 20%; Darryl Smith, PI: 20%; Athanasios Chantis, PD: 40%

Interactions:
Internal - National High Magnetic Field Laboratory (S. Crooker), Center for Integrated Nanotechnology (A. Balatsky, S. Tretiak, S. Picraux, A. Taylor), Los Alamos Neutron Science Center (M. Fitzsimmons), Theoretical Division (A. Saxena, E. Batista)
External - University of Cambridge (P. Littlewood, R. Friend, H. Sirringhaus), UC Santa Barbara (A. Heeger, G. Bazan, Q. Nguyen, C. Palmstrom), U Minnesota (P. Ruden, P. Crowell), Johns Hopkins U (H. Katz), U Florida (F. So)

Related Project URL:
http://ceem.ucsb.edu/about

FWP Title: Nanophosphors: Fundamental Science of Insulators **Los Alamos National Laboratory**
FWP Number:LANLE411 **B&R Code: KC020103**

Program Abstract: In the area of nanophotonics, where the emphasis has been on semiconducting quantum dots, many new optical and electronic properties have emerged. Realization that reduced dimensionality in semiconductors can lead to such exciting new behavior begs the logical scientific question: What physical and chemical behavior can be expected from reduced dimensionality in insulators? This suggests a new subfield—"nanophosphors"— which provides a new arena for fundamental nanoscale studies. To answer the question previously posed we have fabricated simple and complex oxide nanophosphors with a high degree of crystalline phase purity and size control. Theoretical modeling of the temperature and dopant concentration dependence of the lifetime in oxyorthosilicate nanophosphors provide fundamental insights into energy transfer and radiative processes that span timescales from nanoseconds to seconds. We also investigated a unique effect due to reduced dimensionality, i.e. the dependence of nanophosphor emission lifetime on the surrounding medium. Our proposed new research extends the use of core-shell nanostructures for RE doped, luminescent oxides and halides in three novels ways: 1) developing a new class of nanoceramics made from non-cubic nanophosphors, 2) isolating and controlling nanophosphor surfaces to develop a fundamental scientific understanding of how disorder affects surface luminescence phenomena 3) studying energy transfer between RE ions in nanophosphors. This proposed work strongly supports DOE's Office of Science focus on nanoscience discovery, development of fundamental scientific understanding, and conversion of this knowledge into useful technological solutions that benefit the nation.

Program Impact: Our interest in nanophosphors has led us to investigate lanthanide halide nanoparticles, which have the highest reported energy conversion efficiency for converting ionizing radiation into electromagnetic radiation; i.e. scintillation. This is primarily due to the high transport efficiency of electron-hole pairs to recombination sites within the crystal, which is a consequence of their low phonon energies, as compared to oxide nanoparticles. These materials are of interest in furthering our fundamental understanding of phonon confinement effects and energy transport mechanisms in nanocrystals and show interesting effects such as lattice relaxation at particle sizes below 100 nm, surface luminescence, and phonon confinement. Unfortunately, severe hygroscopicity and chemical reactivity has precluded controlled synthesis of these materials in nanoparticle form. Our unique experience (world-class colloidal and lanthanide chemistry expertise through CINT and Chemistry Division) and our extensive characterization and synthesis capabilities, including a dedicated glovebox laboratory for nanomaterial processing, makes our team well qualified to undertake this research. Central to developing a successful synthetic approach is improving our detailed understanding of the bonding and orientation of the ligand shell by the use of small angle x-ray and neutron scattering, which is enabled by close collaboration with LANSCE.

We expect this research to significantly contribute to DOE-BES programs because understanding energy transfer processes at the nanoscale is a central theme to several BES research programs.

FY 2009 Authorized Budget (New BA): $350,000

Program Personnel Supported in FY2009:
Ross Muenchausen, PI (30%)
Michael Blair, co-I (20%)
Nick Smith, PD (30%)
Bryan Bennett, Tech. support (20%)
Stephanie Tornga, student (30%)
Chris Stanek , co-I (10%)

Interactions:

Dr. Marvin Warner	PNNL	Spin interaction in quantum dots
Prof. Antonio Gomez	Univ. Fed. do Ceará	Defects in ferroelectrics
Prof. Eduardo Yukihara	Okla. St. Univ.	Luminescence of nanophosphors
Prof. Peter Rez Drs. Matthias Graf, Darryl Smith, & Rich Martin	Ariz. St. Univ. LANL	Charge transport mechanisms
Drs. Kurt Sickafus & Blas Uberuaga	LANL	Defects in nuclear waste forms
Dr. Markus Hehlen	LANL	Phonon effects in nanophosphors
Dr. John Gordon	LANL	Synthesis of nanophosphors
Drs. Kate Page & Thomas Proffen	LANL	Neutron PDF for nanophosphors

FWP Title: Complex Electronic Materials **Los Alamos National Laboratory**
FWP Number: LANLE415 **B&R Code: KC020201**

Program Abstract:

Competing interactions that non-linearly couple spin, charge, and lattice degrees-of-freedom create complex behavior and collective states with functional responses on multiple length and time scales. A delicate balance of interactions leads to near degeneracy of broken-symmetry ground states, transitions between them, and transitions to complementary uniform states and can be tuned by slight changes in sample composition/dimensionality, temperature, pressure/stress or magnetic field. This complex behavior is most pronounced near the magnetic/non-magnetic and metal/insulator boundaries in materials where electronic correlations are particularly strong. Research focuses on developing a fundamental understanding of the physics of complex electronic materials, especially highly correlated f-electron systems, by discovering and exploring new materials that reveal essential new physics and by applying a necessarily broad range of experimental techniques.

Program Impact:

Developing an understanding of complex electronic materials and their quantum phenomena requires a broad perspective. The discovery of new complex electronic materials has played a significant role in shaping perspective and in driving the discovery of new physics. Exploration of new materials, often in single-crystal form, is a central theme of this project, but success only is possible by fully integrating the discovery of new materials with a necessarily broad suite of readily available experimental techniques. An overview of the macroscopic properties of new materials, which often identifies new physics, comes from rapid turn-around (charge and heat) transport, magnetic, and thermodynamic measurements over a wide temperature range; whereas, in-depth microscopic probes of spin-charge-lattice dynamics of the ground states and their excitations are provided by photoemission spectroscopy, inelastic neutron scattering, and nuclear quadrupole/magnetic resonance techniques, which span complementary time and length scales. Many of the macroscopic and microscopic measurements are made at extremes of very low temperatures, high magnetic fields, and high pressures. Capabilities of the Los Alamos Manuel Lujan Neutron Scattering Center (MLNSC) and National High Magnetic Field Laboratory (NHMFL) Pulsed Field Facility are particularly valuable in this research. Collectively, this suite of integrated techniques has proven effective, as witnessed by the internationally recognized leadership of this project in creating new science through the discovery and study of new correlated electron materials and new quantum states of matter that emerge in them.

FY 2009 Authorized Budget (New BA): $1,200,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):

PI.s: J. D. Thompson (30%), W. Bao (15%), E. D. Bauer (40%), R. Movshovich (30%), E. Nazaretski (25%), F. Ronning (40%), J. L. Sarrao (10%); PDs: S. Baek (40%), K. Gorfyk (20%), N. Kurita (30%), H.-O. Lee (50%), C. Miclea (50%), P. Tobash (20%) Y. Tokiwa (30%)

Interactions: (limit to current interactions and collaborations)

Z. Fisk (University of California, Irvine), C. Booth (Lawrence Berkeley), J. M. Lawrence (University of California, Irvine), A. Bianchi (University of Montreal), M. Kenzelmann (ETH/PSI), C. Broholm (Johns Hopkins University), C. Stock (ISIS), A. Yazdani (Princeton), D. Mandrus (Oak Ridge National Laboratory), H. Sakai (Japan Atomic Energy Agency, Tokai), S. E. Brown (University of California, Los Angeles), F. Steglich, S. Wirth, O. Stockert and M. Nicklas (Max-Planck Institute for Chemical Physics of Solids), Peter Oppeneer (Uppsala), Hidekazu Okamura (Kobe University) ,G. Lander (Institute Laue Langevin), V. Sidorov (Institute for High Pressure Physics, Troitsk), P. Pagliuso (UNICAMP), D. Pines (University of California, Davis), and L. Greene (University of Illinois). Extensive use is made of the Manuel Lujan Jr. Neutron Scattering Center and the NHMFL.

Related Project URL: (optional) N/A

FWP Title: Complex Electronic Materials **Los Alamos National Laboratory**
FWP Number: LANLE415 **B&R Code: KC020201**

Program Abstract:

The electronic structure of transuranic materials is investigated using photoelectron spectroscopy. A broad range of strongly correlated electronic properties (magnetism, superconductivity, enhanced mass, Mott transitions) are manifest in actinide materials with several of the most interesting properties centered around plutonium. The 5f electrons in plutonium play a central role in the emergent properties of Pu metal, alloys and compounds. Through the use of angle-integrated, angle-resolved, and core-level photoemission, this program advances fundamental understanding of the emergent character of 5f properties. Plutonium and other transuranic materials research is conducted at Los Alamos while lighter actinide research is carried out at public synchrotrons. This program looks for systematics in electronic properties across families of strongly correlated materials (UO_2, NpO_2, PuO_2; UTe, NpTe, PuTe; $CeCoIn_5$, $UCoGa_5$, $PuCoGa_5$) focusing on transuranic materials which cannot be measured elsewhere.

There are opportunities to understand the fundamental nature of strong correlations which are uniquely accessible in transuranic materials thus warranting the added complications of research with transuranic materials. In the area of superconductivity, the Pu superconductor $PuCoGa_5$ has a superconducting transition temperature an order of magnitude larger than its Ce counterparts and provides an opportunity to connect the understanding of superconductivity between the cerium and uranium heavy fermion superconductors with the cuprate superconductors. In the area of Mott insulators, the actinide dioxides are a family of insulators where the electronic structure is consistent with ionic solids in the lighter actinides but moves to hybridization and covalency as one approaches PuO_2. The transition between ionic and covalent or, the hybridization between the 5f electrons and O 2p bands is best observed in PuO_2 where hybrid functional theory predicts maximum hybridization . Actinides represent the middle ground between itinerant transition metals and localized rare-earth metals. This middle ground often provides exceptional opportunities for enhanced understanding. Within the actinide materials, uranium research has been exploited to a large degree but plutonium is often found to be the region of actinide interest with the most exceptional electronic structure. Through photoelectron spectroscopy of transuranic materials, we provide a unique perspective on the electronic structure of strongly correlated materials.

Program Impact:

This program makes use of the unique facilities and capabilities for transuranic research at Los Alamos National Laboratory (LANL) including single crystal compound growth via flux growth method as well as thin film capabilities using polymer assisted deposition. Alloys and elemental Pu are also available through unique sample preparation facilities at LANL. This subtask leverages new materials discovery from the parent program (Complex Electronic Materials) and exploits the transuranic capability to add critical detail in the cross-over region of 5f character from itinerant to localized behavior. Characterization and samples obtained from the parent program are used for detailed spectroscopy in this program. The program also takes advantage of the strong theory and modeling effort available for 5f electron materials at LANL. At the present time, this program provides the only angle-resolved photoemission capability for transuranic materials in the world. The program also provides the only transuranic tunable vacuum-ultraviolet photoemission capability in the world. Beyond the interesting fundamental physics which is opened up by plutonium research, the DOE has strong programmatic drivers in the areas of environmental remediation, disposition of spent nuclear fuel, as well as current and next generation nuclear fuels.

FY 2009 Authorized Budget (New BA): $300,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):

J.J. Joyce, PI and staff member (30%), T. Durakiewicz, staff member (20%), K.S. Graham, research technologist (20%)

Interactions: (limit to current interactions and collaborations)

External collaborators; C.G. Olson (Ames Lab, now deceased), P. Riseborough (Temple University), P. Oppeneer (Uppsala University), internal collaborators outside current group; Jian-Xin Zhu, (T-4), John Wills (T-1), Rich Martin (T-1), David L. Clark (Seaborg Institute), Q.X. Jia (MPA-CINT).

Related Project URL: (optional)

FWP Title: Complex Electronic Materials **Los Alamos National Laboratory**
FWP Number: LANLE415 **B&R Code: KC020201**

Program Abstract:

A recent discovery that magnetic fields and X-ray beams can alter the magnetic and conducting properties of *chemically homogenous* complex oxides by writing or painting with strain suggests the possibility that in circuits might be written into films with strain. Key to writing electronic (or spintronic) structures is to understand how changes of strain and structure induced in a chemically homogenous film lead to new functionality. Is new functionality intrinsic to the complex oxide? Is functional behavior observed in bulk complex oxides seen in their thin film cousins? The influence of epitaxial strain (i.e., strain arising from the lattice mismatch between a film and its substrate, as opposed to "written" strain just described) on the average magnetic structure and properties of complex oxide thin films is well-documented. Epitaxial strain is non-uniform and difficult to systematically control without affecting other factors (e.g., film texture, etc.). Therefore, if we wish to learn how strain and magnetic/electronic properties interact, a new experimental approach is needed. Our goal is to acquire data taken with nanometer spatial resolution as we systematically apply stress to a sample. These data are needed to test and further develop theories of non-linear phenomena (i.e., functional behavior) in complex oxides.

We are pursuing two examples of functional behavior. First, we will apply neutron and x-ray scattering techniques to characterize coexistence of magnetic-metallic and non-magnetic-insulating phases in manganite thin films. We will develop a means to apply pure bending stress to films and observe how phase coexistence is affected. Our observations will provide important information to test the Ahn-Lookman-Bishop theory of this phenomenon. Second, we will investigate whether the interface between two non-magnetic materials $LaAlO_3$ and $SrTiO_3$ is magnetic as has been recently suggested. A direct and quantitative measurement of the magnetic moment and its spatial extent across the $LaAlO_3$/ $SrTiO_3$ interface will provide insight into the nature of magnetism at interfaces between dissimilar complex oxides. For example, depending upon the magnitude of the effect, we might be able to discern whether the magnetism arises from electrons trapped at the interface, or from diffusion of Ti across the interface and concomitant change of valence.

Program Impact:

Numerous groups have investigated the influence of substrate-choice on the electronic and magnetic properties of complex oxide films, e.g., to understand the role of epitaxial strain on complex oxides. These studies have had successes; however, it is difficult to discriminate between the influence of film growth mode (determined by the substrate) and epitaxial strain on the resultant properties of the films. Our approach aims to systematically apply stress to the film's substrate in order to understand how the resulting strain in the film affects its magnetic properties. To achieve our goals we require high quality samples, a method of imposing controlled strain on our samples, and a means to measure magnetic and atomic structures with micron or better resolution. Since our effort is very modest, we have partnered with colleagues who grow samples. We have taken advantage of expertise in MST-CINT to develop techniques to apply stress and measure strain in our samples. Magnetic and atomic characterization of samples has been performed at the Lujan Center, the SNS, NIST, APS and NSLS through their respective user programs.

Coexistence of ferromagnetic-metallic and charge-ordered antiferromagnetic (or paramagnetic) domains (phase coexistence) is well established in *bulk* manganites. Phase coexistence has been found in cobaltite thin films using combinations of magnetometry, transport and neutron scattering. Unusual transport behavior in thin film manganites has been attributed to phase coexistence by at least two groups. However, to our knowledge "smoking gun" evidence of phase coexistence in manganite thin film is still lacking. Using neutron and resonant x-ray scattering, we have looked for phase coexistence in length scales spanning 10 to 300 nm and 1 to 10 μm. While we observe magnetism, we have yet to observe evidence for scattering to support claims of phase coexistence in thin manganite films.

FY 2009 Authorized Budget (New BA): $250,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:
25% M.R. Fitzsimmons (P.I.), 100% J. Olamit (postdoc)

Interactions: (limit to current interactions and collaborations)
J. Thompson , Y. Wang , N. Hengartner, A. Biswas, J.A. Borchers, C. Sanchez-Hanke, J. Budai, I.K. Schuller, J. Santamaria, A. Brinkman, D. Schlom (Cornell)

FWP Title: Quantum Electronic Phenomena and Structures **Los Alamos National Laboratory**
FWP Number: LANLE301 **B&R Code: KC020202**

Program Abstract:
The overall goal of this project, undertaken in collaboration with researchers at Sandia National Laboratories and the University of New Mexico, is to explore novel quantum phenomena in unique low-dimensional semiconductor structures. The project is divided into two subtasks, one focusing on quantum transport in structured semiconductors and the other examining the growth and properties of III-V (particularly nitride) nanowires. LANL's role in this project, primarily in conjunction with the second subtask, is to use our advanced ultrafast optical capabilities to characterize carrier dynamics in semiconductor nanowires as a function of various experimental and fabrication parameters, with the goal of elucidating novel phenomena in these quasi-one-dimensional systems. To date, we have primarily focused on measurements of ultrafast dynamics in ensembles of GaN nanowires, where we have revealed the influence of defect states on the relaxation of photoexcited carriers in these systems [1]. This, in conjunction with our previous work on other nanowire systems such as Ge and CdSe, underlines the importance of surface and bulk defect states in governing the properties of semiconductor nanowires [2]. We are currently exploring methods (e.g. radial (core/shell) heterostructuring) of minimizing the influence of defect states in GaN nanowires, and are also exploring the extension of ultrafast optical experiments to the single nanowire level, in order to remove the inhomogeneous broadening inherent to ensemble measurements. Ultrafast optical experiments on single nanowires may also enable us to temporally and spatially resolve carrier transport in these systems on a sub-100 femtosecond time scale and sub-micron length scale, which will give substantial insight on their unique properties.

[1] P. C. Upadhya, Q. Li, G. T. Wang, A. J. Fischer, A. J. Taylor, and R. P. Prasankumar, "The influence of defect states on non-equilibrium carrier dynamics in GaN nanowires," **(invited)** *Semiconductor Science and Technology* (special issue on NWs), **25**, 024017 (2010).
[2] R. P. Prasankumar, P. C. Upadhya, and A. J. Taylor, "Ultrafast dynamics in semiconductor nanowires," **invited review article,** *Physica Status Solidi (b)*, **246**, 1973 (2009). (cover article)

Program Impact:

This program requires advanced sample growth and characterization capabilities, which necessitates access to multiple facilities and the involvement of different investigators with expertise in both sample fabrication and different characterization techniques (e.g., scanning electron microscopy, photoluminescence, ultrafast optical spectroscopy). These investigators must work together to make progress in understanding the complex phenomena that are revealed in these experiments on low-dimensional semiconductor structures.

FY 2009 Authorized Budget (New BA): $140,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):
Co-investigator: Rohit Prasankumar, 0.15 FTE
PD: Prashanth Upadhya, 0.5 FTE

Interactions: (limit to current interactions and collaborations)
SNL staff: Wei Pan, George Wang, Art Fischer, Mary Crawford
SNL PD: Qiming Li

Related Project URL: (optional)

FWP Title: Science of 100 Tesla **Los Alamos National Laboratory**
FWP Number: LANLF100 **B&R Code: KC020202**

Program Abstract:
We are performing a coordinated basic research program using our unique capability to produce millisecond-duration fields of 100T to study high-magnetic-field-induced phase transitions and the effects of nano-quantization. Each of the experiments performed is of overwhelming importance, demonstrably feasible, and cannot produce useful results in fields lower than 80 T. We include the areas of physics traditionally explored in high-field pulsed magnets, with a mix such that we shall advance substantially our understanding of condensed matter. Our aim is to reveal new and striking physics.

Program Impact:
A 100T, millisecond magnetic field (11meV/spin, 130K) is a unique stimulus capable of selectively perturbing thermodynamic balance. 100T magnetic fields can force electronic energy levels to cross in 4f and 5f elements, as well as those made observably discrete in nano-scale systems. Each crossing creates a phase transition that can be used as a quantitative test of many theories. 100T magnetic fields can also change fundamental behavior by suppressing the relative importance of disorder. The observation of dHvA oscillations, aided by the exponential increase in signal-to-noise ratio with magnetic field, and the stunning reentrant behavior of certain dissipation mechanisms, observed in resonance-width via optical techniques, are nano-scale quantum effects that will expand our understanding of very fundamental and ubiquitous processes in condensed matter. The 130K energy of a 100T field is sufficient to destroy superconducting, charge-density-wave, and Kondo-induced gaps, cleaning out the gap-induced order to leave behind the physics beneath the energy gap. Such investigations were key to establishing the exponential freeze-out of normal electrons in BCS superconductors.

This year, the 100 T magnet was run as an integral part of the NHMFL user program supported by the NSF, with in excess of 100 shots to ~85 T provided for science: no such capability exists elsewhere in the world. In spite of significant demand for magnet time, requests submitted locally (by the "100 T Science" team) had by far the greatest success in yielding exciting new experimental results, particularly on Fermi surface properties and related phenomena in high temperature superconductors: topics that were an integral part of this proposal. This demonstrates that major breakthroughs necessitate having a team of scientists on location dedicated to the pursuit of high magnetic field science with long established expertise. A substantial fore-knowledge of which experiments are most likely to work or yield significant results provides a significant advantage in planning experiments, developing new experimental techniques and bringing in external collaborations.

FY 2009 Authorized Budget (New BA): $835,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):
N. Harrison (PI), 30%; J.Singleton (co-I), 50%; A. Migliori (co-I), 10%; F. F. Balakirev (co-I); 30%; R. D. McDonald (co-I), 20%; J.B.Betts (co-I), 20%; D. G. Rickel (staff scientist), 10%; Suzuki (postdoc), 10%; Wang (technician), 10%; Gordon (technician), 10%.

Interactions: (limit to current interactions and collaborations)
Suchitra Sebastian & G. G. Lonzarich (University of Cambridge, England); P. A. Goddard (University of Oxford, England); J.L.Manson (Eastern Washington University); E. Bauer (Los Alamos National Laboratory); J. A. Mydosh (Univ. Nijmegen, Netherlands); G. S. Boebinger (Florida State University); W. Halperin (Northeastern University); P. Dai (University of Tennessee/ Oakridge).

Related Project URL: (optional)

FWP Title: Toward a Universal Description of Vortex Matter **Los Alamos National Laboratory**
FWP Number: LANL1092 **B&R Code: KC020202**

Program Abstract:

Vortex physics became a major field in condensed matter and statistical physics since the discovery of the oxide HTS. Although the rich HTS vortex phenomenology arises from the large influence of the thermal fluctuations, there is no hard boundary between HTS and LTS, thus a comprehensive vortex matter description should be universal. However, interactions of vortices with material defects, which produce *pinning*, have been considered too complex and material dependent to be described in a general framework. We will challenge this concept. Taking a fundamental science approach, we will develop a description of vortex matter in the presence of inhomogeneities, including flux pinning and creep phenomena, valid for all superconductors. By comparing and contrasting systems with vastly different properties under a broad spectrum of conditions including extreme ones, and by improving theoretical models, we will establish a general picture that cannot be obtained by studying individual systems. This will drastically enhance our capability for predicting, controlling and designing the behavior of vortex matter. The relevance of this study goes beyond existing materials, as yet-to-be-discovered superconductors will share most of the vortex physics explored here.

Program Impact:

We at LANL have a unique combination of expertise and facilities to perform this research. We have access to DC and pulsed high magnetic fields at the NHMFL, in particular through the collaboration with the "100 Tesla Science" program. We benefit from knowledge, top quality samples and experimental tools provided by the "Complex Electronic materials" program, and the significant infrastructure and experience in superconducting thin films fabrication within the Office of Electricity Delivery and Energy Reliability program at the STC. We are also establishing several collaborations, both inside and outside LANL, to obtain high quality samples of several superconducting materials. Finally, we can interact with a significant number of condensed matter theoreticians working at LANL.

FY 2009 Authorized Budget (New BA): $650,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):

STAFF:

Leonardo Civale (PI)	60% FTE
Boris Maiorov	25% FTE
Lev Bulaevskii	10% FTE
Igor Usov	10% FTE

POSTDOCS:

Nestor Haberkorn	100 % FTE
Masashi Miura	0% FTE (LANL Director's Fellow working on this project)

VISITING SCIENTIST:

Arkadi Shekhter	Postdoc at Universiy of Florida, visiting LANL for 2 months, mentored by L. Bulaevskii.

Interactions: (limit to current interactions and collaborations)

- Group of Prof. H. Hosono, Tokyo Institute of Technology, Japan.
- Group of Prof. Paul Canfield, AMES and Iowa State University.
- Group of Prof. Judith Driscoll, University of Cambridge, UK.
- Dr. Evgueni Nazaretski, BNL.
- International Superconductivity Technology Center (ISTEC), Japan.
- Dr. Tsuyoshi Tajima, AOT-MDE, LANL.
- Group of Prof. Tsuyoshi Tamegai, University of Tokyo, Japan.
- Dr. Paul Clem, SNL.

Related Project URL: (optional)

FWP Title: Integrated Modeling of Novel Materials **Los Alamos National Laboratory**
FWP Number: LANLE304 **B&R Code: KC020203**

Program Abstract:
Complex electronic materials are of great scientific interest. These materials exhibit strong electronic correlations along with strong electronic coupling to multiple degrees of freedom, like lattice and spin. New tools, such as the Scanning Tunneling Microscope (STM) and the Atomic Force Microscope (AFM) were applied to these materials. They reveal substantial spatial inhomogeneity in high-*Tc* cuprates and manganites and possibly in heavy fermion materials. Electronic inhomogeneity in these materials appears to be a more common occurrence than we thought earlier. Theoretical understanding of the role of inhomogeneity, coupling to spin and lattice degrees of freedom and competition between different phases in these materials is a crucial missing step in our understanding of these materials. The overarching goal of the project is to provide an understanding of the fundamental physical processes that determine nanoscale inhomogeneity and coupling between various degrees of freedom in correlated electronic materials. Physical processes of interest include: drivers and mechanisms of inhomogeneity, coupling to local lattice and spin degrees of freedom, transport and dynamics. Our goals are to discover new laws that govern the behaviour of states of matter and to create the essential new understanding and interpretative framework demanded by these discoveries. We will further develop numerical and analytic methods that will make possible detailed analysis and predictions about specific experimental properties. Ultimately we would like to use the theoretical understanding developed in this work to predict and develop new functionalities in these materials.

Program Impact:
Electronic materials that are being investigated today are complex, and typically exhibit competing phases, sensitivity to small changes in control parameters, and enhanced sensitivity to disorder. This competition and sensitivity often results in nanoscale inhomogeneity. In materials such as cuprate superconductors and in manganites, the electronic inhomogeneity is believed to be a reflection of competition between phases but at the same time is playing a crucial role in the creation of unusual and practical properties of these materials. Understanding the mechanisms and origins of electronic correlations, inhomogeneity, coupling to local degrees of freedom and its subsequent control in bulk materials, films and in artificial structures requires new theoretical approaches and conceptual frameworks. In our study we apply advanced modeling and simulation tools, like mean field, ab initio calculations to describe properties of materials, interpret and guide modern experimental probes of multiple spatial and temporal scales, including high magnetic fields, ultrafast time-resolved optical and scanning-tunneling microscopies.

Our primary goal is to discover new laws that govern the behavior of materials at local length scale and short time scale in the presence of strong electron-lattice-charge coupling and to create the new methods that would adequately describe these materials. Understanding of emergent behavior in materials with multiple, competing interactions is required for the controlled design and creation of materials with desired characteristics. This research is directly impacting LANL's and DOE's mission on Discovery science in novel materials and phenomena. Variety of methods we use requires a diverse team approach. Our theoretical work is strongly coupled to the ongoing experimental work on correlated materials at Los Alamos at CINT, National High Magnetic Field Laboratory and Lujan Center.

Our work is having a major impact on strongly correlated electron research that has lead to major collaboration with UCSD, UC Berkeley, UC Davis and Cornell U. Members of the team are serving at the major international conferences: Advisory board for Spectroscopies of Novel Superconductors(http://www.sns2010.org/) , Quantum Fluids and Solids (http://qfs2010.neel.cnrs.fr/spip.php?rubrique1), organizing committee for 2010 Asia Pacific Center for Theoretical Physics Conference on Frontiers in Electronic Quantum Matter (http://www.apctp.org/conferences/FEQM/winter2010commitee.html), and organizing committee for SCES 2010, International Conference on Strongly Correlated Electrons Systems (http://sces.newmexicoconsortium.org/).
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FY 2009 Authorized Budget (New BA): $380,000
Program Personnel Supported in FY2009:
A. V. Balatsky 10% -PI, R. C. Albers 10%-PI, S. Trugman 10%-PI, J.X. Zhu 10%- PI, M. Graf- 10%, Y. Dubi – 50%- PD.
Interactions: (limit to current interactions and collaborations)
C. Batista(T-4), D. Smith (T-4), CINT (S. Tretiak, Q. Jia, A. Taylor). Outside: J.C. Davis (Cornell), D. Basov(UC San Diego), Jan Zaanen(Leiden), N. Curro(UC Davis), M. Crommie(UC Berkeley), Q. Si (Rice), N. Christensen and Axel Svane (Aarhus University), N. Harrison (MPA-CMMS), S. Sebastian (U. Cambridge).
Related Project URL: http://theory.lanl.gov

FWP Title: Accelerated Molecular Dynamics Methods **Los Alamos National Laboratory**
FWP Number: LANL1110 **B&R Code: KC020203**

Program Abstract:
Molecular dynamics (MD) simulation, a powerful tool for probing systems in full atomistic detail, is limited to nanoseconds, while activated processes that govern material evolution take place on much longer time scales. Moreover, most real systems have a complexity that makes it difficult or impossible to accurately predict their dynamical evolution using intuition or simple models. Accelerated molecular dynamics methods, developed primarily under this BES funding over the last dozen years at Los Alamos, offer a way out of this dilemma. Built on solid statistical mechanical concepts, these methods follow the long-time evolution of activated processes in full, accurate detail. We can reach time scales of milliseconds, seconds and beyond, and we invariably observe complex, unanticipated behavior, even in seemingly simple systems. We are applying these methods to assist other DOE programs at LANL, and developing the methods further to make them applicable to the widest possible range of problems. In particular we are developing new algorithms for getting around the low-barrier problem, treating more complex systems, and making use of massive parallelism. We teach courses and give tutorials on these methods at international venues. We are developing user-friendly software and collaborating on applications with experts from around the world. Feedback from the collaborations in turn shows us where further development is most needed.

Program Impact:
The accelerated molecular dynamics (AMD) concept, that the best way to evolve a system from state to state is to let the trajectory find its own way out of each state, is impacting the way scientists view infrequent-event systems and activated processes. AMD simulations here and elsewhere are elucidating key mechanisms in processes such as surface diffusion, vapor-deposited crystal growth, bulk diffusion, radiation damage annealing, carbon nanotube dynamics, grain boundary shear, metallic void growth/transformation, and nanocluster dynamics. Implementations of the AMD methods are starting to appear in widely-used atomistic simulation packages developed outside LANL (e.g., DL_Poly and now LAMMPS), and the AMD concepts are being taught in international courses. Within Los Alamos, this core program on AMD methods has become a powerful hub of expertise and development that provides beneficial interactions with various programmatic efforts [e.g., programs on advanced nuclear fuels and waste (e.g., GNEP/AFCI), the ASC Enhanced Surveillance program, the BES program on radiation damage in ceramic materials, fusion materials research under OFES, and the Open Science program to exploit the LANL Roadrunner supercomputer] and in some cases has played a role in creating new programs [e.g., the recently funded BES EFRC program at LANL on materials at irradiation and mechanical extremes (PI: M. Nastasi), the SCIDAC program on stress-corrosion cracking (PI: P. Vashishta, USC), and the DOE/ASCR program on predictive simulation and design of materials by quasicontinuum and accelerated dynamics methods (PI: M. Luskin, U. Minn.)]

FY 2009 Authorized Budget (New BA): $310,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):
Arthur F. Voter (PI) – 25%
Danny Perez (LANL Postdoc, converted to LANL staff near end of FY09) – 20%
Chun-Wei Pao (LANL Postdoc) – 35%
Abhijit Chatterjee (LANL Postdoc) – 20%
Antonio Cadilhe (Visitor on Fellowship from University of Minho, Portugal) – living expenses.

Interactions: (limit to current interactions and collaborations)
Blas Uberuaga, Sriram Swaminarayan (LANL)
Programs and centers mentioned above in Program Impact section
Jacques Amar and his group (University of Toledo)
John Hamilton and his group (Sandia National Laboratory, CA)
Ashlie Martini and her group (Purdue)
Adrian Roitberg and his group (U. Florida)

Related Project URL: (optional)

FWP Title: Cooperative Phenomena in Molecular Nanocomposites **Los Alamos National Laboratory**
FWP Number: LANLE307 **B&R Code: KC020203**

Program Abstract:

The purpose of this program is to establish key scientific principles needed to design and fabricate molecular nanocomposite materials that integrate functional molecular, and in some cases biomolecular, components within rigid nanostructured inorganic architectures. The overall project involves a joint effort between researchers at LANL and Sandia National Laboratories (SNL, Albuquerque), which is led by James Voigt and C. Jeff Brinker. Our work in this program includes the development of methods to create patterned and functionalized nanoporous silica thin films, as well as the creation of new bulk materials incorporating active molecular and biomolecular components into nanostructured silica materials. In many cases, such materials are multifunctional and can exhibit unexpected emergent behaviors that are potentially useful for sensing and analytical characterization applications.

Program Impact:

The "Molecular Nanocomposites" Program at Los Alamos National Laboratory (LANL) greatly benefits from interactions with other DOE-BES funded programs. In particular, expertise and equipment located in the Center for Integrated Nanotechnologies, a DOE-BES funded user facility colocated at LANL and SNL, has allowed us to expand the techniques we use to characterize the molecular nanocomposite materials prepared in our program. In addition, we have significant interactions with Andrew P. Shreve, PI on a DOE-BES funded program at LANL, whose spectroscopic expertise has significantly helped us gain a better understading about the materials prepared under our program.

FY 2009 Authorized Budget (New BA): $80,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):

Andrew M. Dattelbaum, PI, 0.2 FTE

Interactions: (limit to current interactions and collaborations)

C. Jeff Brinker, Sandia National Lab/University of New Mexico
Andrew P. Shreve, Los Alamos National Laboratory

Related Project URL: (optional)

FWP Title: Molecularly Engineered Biomimetic Nanoassemblies **Los Alamos National Laboratory**
FWP Number: LANLE308 **B&R Code: KC020301**

Program Abstract:
The program aims to develop self-assembly and biologically-assisted assembly methods for the control of functional responses in complex, multi-component materials. Relevant functions being explored are related to the control of energy flow and transduction, and include photophysical properties, charge-transfer processes, and manipulation of bioenergetic responses including those mediated by molecular recognition events. Focus on these functions and on use of a few active components, selected to represent several different classes of important nanomaterials, is intended to also provide improved general understanding of structure and performance of the assembly types under study. The approaches used include a combination of materials synthesis and fabrication, static and time-resolved spectroscopies, optical and scanning probe microscopies, structural characterization, and modeling and analysis. The research team includes personnel with expertise in chemical and materials synthesis, self-assembly, electrochemistry, spectroscopy, molecular biology and biochemistry, and structural characterization.

Program Impact:
The program has generated improved understanding of how to control complex self assembly processes to create functional nanoscale materials. Applications of such materials are found in energy production and storage, catalysis, and sensor technologies. The multiple investigator nature of the program enables the study of such assembly methods across several classes of materials ranging from conjugated polymers to biological membranes. Also, the breadth of capabilities allows the application of a variety of characterization tools, including those within BES-supported user facilities at Los Alamos (the Center for Integrated Nanotechnologies and the Los Alamos Neutron Science Center).

FY 2009 Authorized Budget (New BA): $730,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE (Clearly delineate status of individual: PI, PD, student. Technical Support Staff):
A.P. Shreve (10%, PI); H.-L. Wang (20%, co-I); J.S. Martinez (10%, co-I); S. Iyer (20%, co-I); R.C. Rocha (10%, co-I); S.H. Jeon (100%, student); C. Korman (20%, student); H. Yoo (50%, postdoc)

Interactions: (limit to current interactions and collaborations)
Atul N. Parikh (UC Davis); James A. Brozik (Washington State University); Darryl Sasaki (Sandia National Laboratories); Sunil Sinha (UC San Diego).

Related Project URL:

FWP Title: Hydroxide Conducting Systems Fuel Cells **Los Alamos National Laboratory**
FWP Number: LANLE312 **B&R Code: KC020301**

Program Abstract:

The vision of a Hydrogen Economy is compelling for reasons of improved energy security and environmental impact; however, before such a vision can be met there are major technological barriers that must be overcome. Namely, commercially viable technologies for the production (electrolyzers) and the use (fuel cells) of hydrogen must be developed. Hydroxide conducting systems can be used for either production or use of hydrogen and offer specific advantages compared to competing technology. To date, investigation of hydroxide conductors for fuel cells or electrolyzers has been limited due to perceived limitations of durability, conductivity and/or carbonate formation. Our program, a joint effort between LANL and NREL, combines experts in the area of fuel cells, synthetic chemistry and modeling to elucidate decay mechanisms and design new chemical structures to overcome them. The primary advantage of hydroxide conductors is the enablement of non-precious metal catalysis, a critical showstopper to widespread implementation of traditional (acidic) fuel cells and a potential advantage for electrolyzers. We have used chemical and thermal degradation studies of target cations for use in anion exchange membranes (AEMs) to elucidate the degradation mechanisms and rates of target cations and correlated these studies with computational studies. These studies have shown the unexpected importance of ylide formation as a degradation pathway, the role of water (solvating media) in stabilizing cations, and have explored cations with increased stability. While membranes using the standard tetraalkyl ammonium cations have been reported to show poor stability at even 60C, we have found that representative cations of these membranes show reasonable stability at much higher temperatures when sufficiently high water contents are present. Recent advances in AEM durability have been reported that are in reasonable agreement with our experimental studies of cation durability, suggesting current AEMs may have the durability required for some limited applications. A specific cation featuring an ether linkage showed approximately 4x improved durability in accelerated testing.
We have begun studies involving carbonate and bicarbonate in these systems as these species will be present whenever carbon dioxide is present and appear to be a potential limiting factor in the performance of AEMs.

Program Impact:

The work has led to significant advances in the field, improving quantification of cation stability and showing AEM based devices can have durability requisite for specific commercial applications. We have shown three, specific cations have improved base stability compared to the standard benzyl trimethyl ammonium cation typical used in AEMs. We have identified cation decomposition mechanisms that have been previously unknown for these material. This knowledge will be used to guide the design of anion exchange membranes in the future and will There has been significantly increased effort by the research community being placed toward anion exchange membranes since this project was initially funded, and this project has played a meaningful role in stimulating this increased interest. For example, a workshop chaired and organized by the project PI has led to an Army Research Office Multi University Research Initiative Request for Proposals that is currently in the review stage.

FY 2009 Authorized Budget (New BA): $130,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE

James Boncella(co-PI) 10%, Joseph Edson (Post-doc) 15%.

Interactions: (limit to current interactions and collaborations)

This project began at Los Alamos National Laboratory (LANL). The PI for the project (Bryan Pivovar) joined NREL but maintained interactions with Jim Boncella and Shaji Chempath at LANL. Collaborations with Cellera, Inc., Diahatsu, Colorado School of Mines, Penn State University and University of California-Riverside.

FWP Title: "Giant" Nanocrystal Quantum Dots: Controlling Charge Recombination Processes for High-Efficiency Solid-State Lighting
FWP Number: LANL1096

Los Alamos National Laboratory
B&R Code: KC020301

Program Abstract: Multiple technical challenges stand in the way of achieving robust, high-efficiency solid-state lighting (SSL). These were summarized in the report of the DOE-BES Workshop on SSL (2006) in terms of two *Science Grand Challenges*: (1) *The need to develop the fundamental understanding of light-emitting materials and nanostructures toward rationally designed SSL structures from the ground up*, and (2) *The need to control the competing pathways by which electricity is converted into light*. Here, we directly address both of these Science Grand Challenges. We establish the fundamental knowledge necessary to develop a new class of emitting nanostructures that will serve as high-efficiency, robust "building blocks" for rationally designed SSL. Furthermore, we base this transformative development on a novel type of semiconductor nanocrystal quantum dot (NQD) – the so-called "giant" NQD (g-NQD) – that affords unprecedented control over excitation→photon conversion processes. Our research is organized around three interrelated Research Goals that deal with fundamental aspects of g-NQD chemistry and photophysics toward a proof-of-principle device demonstration. These Research Goals are summarized as: (I) Understand the precise relationships between g-NQD structure and optical performance toward controlling critical aspects of structure that otherwise lead to non-uniformity in function, (II) Understand the intrinsic and extrinsic g-NQD properties that control carrier recombination processes and eliminate losses in the light-emission process by manipulating these properties, and (III) Demonstrate that the unique g-NQD chemical and photophysical properties translate into significantly improved NQD-LED performance. We envision that this work will build *practical foundations for realizing robust, reduced-cost, high-efficiency SSL technologies.*

Program Impact: The most widely used sources of artificial illumination remain incandescent and fluorescent lamps, but these are not optimized for efficiency or longevity. Significant economic and environmental savings—~20% of electricity is consumed in lighting—could be achieved if efficient and robust low-cost alternatives were available for general lighting purposes. The primary alternative as perceived by industry and government is so-called 'solid-state lighting' (SSL). Its development has become central to DOE's—and our Laboratory's—missions in energy efficiency and security. Current SSL lighting approaches suffer from intricate and costly fabrication methods (and starting materials) and limited emission "colors" (nitride-based light-emitting devices, LEDs) or relatively lower efficiencies and susceptibility to thermal, electrochemical, photooxidative, and environmental degradation (organic or polymer-based LEDs). An ideal "building block" for LED technologies would possess high-efficiency and robustness coupled with low-cost processibility and color tunability. Development of such a building-block material would enable a paradigm change in SSL technology. The interdisciplinary team of co-PIs, Hollingsworth (materials chemistry) and Htoon (single-molecule spectroscopy and photophysics) and the strategic addition of complimentary key personnel [Schaller: ensemble spectroscopy, Werder: electron microscopy/ fabrication, Halas (Rice Un.): plasmonic structures, and Lauhon (Northwestern Un.): 3-D atom probe tomography], combined with the research environment afforded by LANL, promise a significant chance for success in realizing this goal. Specifically, the co-PIs recently pioneered the work on a new "class" of semiconductor nanocrystal quantum dot (NQD) called the "giant" NQD (g-NQD) that may prove to be the next-generation building block for efficient, robust and affordable SSL. g-NQDs exhibit key enabling properties for light-emission applications – significantly suppressed nonradiative carrier-recombination processes, insensitivity to chemical environment/surface chemistry, relatively larger Stokes shift, and high temporal photostability. This prior experience will enable the team to make rapid progress in developing the relevant fundamental science (chemistry and physics) toward a proof-of-concept demonstration of the first truly all-inorganic NQD-based LED for SSL. Critically, both co-PIs are members of the LANL/Sandia Labs DOE Center for Integrated Nanotechnologies (CINT), a Nanoscale Science Research Center (NSRC). Through the CINT, the team has access to a wide array of synthesis, fabrication, and characterization tools. The co-location of complimentary and state-of-the-art facilities and the focus of the national laboratory culture on supporting interdisciplinary research will also be key to the program's success.

FY 2009 Authorized Budget (New BA): $700,000

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:
Hollingsworth (co-PI: 30%), Htoon (co-PI: 25%), Werder (TSM: 10%), Schaller (TSM:10%).

Interactions: (limit to current interactions and collaborations)
Collaborators funded via SISGR subcontract: Prof. Halas (Rice Un.) and Prof. Lauhon (Northwestern Un.). Other project-relevant interactions: V. Klimov (and LANL EFRC personnel), S. Crooker (LANL MPA), S. Ivanov (LANL CINT), Q. Jia (LANL CINT), P. Goodwin (LANL CINT), K. Baldwin (LANL CINT), A. Gin (SNL CINT).