Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and possible subtask under FWP:
Deformation Physics of Ultrafine Scale Materials

FWP Number: SCPE486

Program Scope: 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; micro-tensile, micro-pillar compression and nanoindentation testing; and atomistic and dislocation dynamics simulations of deformation behavior.

Major Program Achievements (program started in FY00, with full funding in FY01)**:**
Nanoscale design of metals with strengths approaching the theoretical limit: An increase of up to two orders of magnitude in strength over bulk materials is observed when the structural scale of the nanolayered composites is reduced to nanometer-scale, e.g., flow strength of approximately 2.5 GPa was measured by micro-pillar compression testing in 5 nm Cu / 5 nm Nb multilayers.
Weak interfaces provide unusually high resistance to slip transmission in nanolayered materials: Atomistic modeling reveals a new strengthening mechanism involving incoherent interfaces: an unusually high resistance to slip transmission originates from dislocation-induced shear of 'weak' interfaces and concomitant dislocation core spreading within the interfaces.
High strength and high radiation damage tolerance: Interfaces act as obstacles to slip and also sinks for radiation-induced defects. Thus, the nanolayered composites exhibit a combination of high-strength and high radiation-damage tolerance.

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. The work from this program is largely the basis for the nanomechanics thrust area in the Center for Integrated NanoTechnologies in New Mexico. The discovery of high radiation damage tolerance will significantly impact the design of structural materials for future nuclear reactors.

Interactions (FY'07):
H.M. Zbib (Washington State University), P.M. Anderson (Ohio State University), A.K. Mukherjee (UC, Davis), I.M. Robertson (University of Illinois), T. Ungar (Eotvos University Budapest, Hungary), M. Uchic (AFRL).

Recognitions, Honors and Awards (since FY'00):
R.G. Hoagland, LANL, Matthias scholar at LANL, FY'00.
P.M. Anderson, Ohio State University, Matthias scholar at LANL, FY'02.
J.D. Embury, 2005 ASM Edward DeMille Campbell Memorial Lecture.
F. Spaepen, 1999 Humboldt Research Award for Senior U.S. Scientists.
F. Spaepen, 2002 Robert Franklin Mehl Award, The Minerals, Metals & Materials Society (TMS).
A. Misra, 2009 MRS Bulletin volume organizer; 2007-08 Chair, Nanomechanical Behavior Committee, TMS.
80 refereed publications, including 3 book chapters; over 35 invited talks at national/ international symposia.
10 symposia organized (MRS Fall 2000; United Engineering Foundation, Italy, 2001; TMS Annual 2003; MRS Spring 2003; TMS Annual 2005; MRS Spring 2004; MRS Spring 2005; MRS Spring 2006, MRS Fall 2006, TMS Annual 2008). Edited 2 journal special issues: Scripta Materialia issue titled *Deformation and Stability of Nanoscale Metallic Multilayers* (March 2004), and MRS Bulletin issue titled *Mechanical Properties of Nanostructured Materials*, 1999.

Personnel Commitments for FY2007 to Nearest +/- 10%:
A. Misra (LANL, 30%), R.G. Hoagland (LANL, 30%), F. Spaepen, (Harvard University, 5%), J.D. Embury (LANL-Affiliate, 10%), J.P. Hirth (LANL-Affiliate, 10%), P. Dickerson (LANL TSM, 20%), A. Donohue (100%, GRA, Harvard University), F. Akasheh (100%, GRA, Washington State University), D. Bhattacharyya (LANL PD, 50%), J. Wang (LANL PD, 100%).

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $729,000 **FY06 BA** $814,000 **FY07 BA** $714,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and/or possible subtask under FWP:
Radiation Damage Effects In Ceramics And Non-Metals

FWP Number: SCPE429

Program Scope: The goal of this program is to understand the radiation damage response of ceramics exposed to neutrons, ions or other energetic particles. Our studies of the damage response of ceramics address two objectives: (1) to predict microstructural evolution in ceramics exposed to radiation; and (2) to identify the physical aspects of ceramics that are effective in promoting radiation resistance. Our ultimate goal is to design new radiation resistant ceramics. We conduct particle irradiation tests on ceramics to evaluate their irradiation damage response. We also perform computer simulations of damage evolution in ceramics to assist in our understanding of radiation damage phenomena in these materials. Our research is focused on highly radiation-resistant ceramics.

Major Program Achievements (over duration of support): Using atomistic computer simulation techniques along with ion beam irradiation experiments on selected oxides, we have demonstrated that certain compounds with crystal structures similar to that of the mineral fluorite are highly resistant to displacive radiation damage. This radiation damage tolerance is very dependent on compound chemistry. For instance, our findings suggest that a large number of isochemical $A_2B_2O_7$ compounds with a structure called pyrochlore (very similar to the fluorite structure, but more highly ordered) should not exhibit resistance to radiation damage, while other $A_2B_2O_7$ compounds should be highly radiation tolerant. The radiation tolerant $A_2B_2O_7$ compounds with the fluorite structure should be suitable hosts for actinide species (Th, U, Pu, etc.). This research was originally published in Science: K. E. Sickafus et al., "Radiation tolerance of complex oxides," Science **289** (2000) 748-751, then recently expounded upon in Nature Materials: K. E. Sickafus et al., "Radiation-induced amorphization resistance and radiation tolerance in structurally-related oxides," Nature Mater. **6** (2007) 217-223. Our theoretical effort has focused on studying the production and evolution of defects in materials under irradiation. Highlighting this work are two publications in Physical Review B: "Atomistic simulations of radiation-induced defect formation in spinels" (PRB **74**, 214105 (2006)) and "Defect kinetics in spinels" (PRB **75**, 104116 (2007))". In addition, we have worked closely with Art Voter to continue development of accelerated molecular dynamics methods, an effort which also led to a number of publications, including "Parallel replica dynamics for driven systems" (PRB **75**, 014301 (2007)), "Reaching extended length scales and time scales in atomistic simulations via spatially parallel temperature-accelerated dynamics" (PRB **76**, 205439 (2007)) and "Direct Transformation of Vacancy Voids to Stacking Fault Tetrahedra" (PRL **99**, 135501 (2007)). These developments will be very helpful in future studies related to this BES program.

Program Impact: Early work on this program laid the foundation for our current understanding of the behavior of model ceramic oxides (such as periclase (MgO) and corundum (Al_2O_3)) in a radiation damage environment. Recent developments on this program have led to an exciting new predictive capability to predict radiation damage evolution in model oxides such as MgO to time scales approaching experimental (order of seconds). Other efforts: Kurt Sickafus organized an international symposium on "Spinel Compounds: Structure Property Relations" at the Annual Meeting of the American Ceramic Society, Cincinatti, OH (1998). The proceedings was published as a special topical issue of the Journal of the American Ceramic Society (Vol. 82(12) 1999). Kurt Sickafus served as Director of a NATO-ASI international school entitled "Radiation Effects in Solids," held in Erice, Sicily in July, 2004. Kurt served as chair the 13th International Conference on Radiation Effects in Insulators, held in Santa Fe, NM, Aug. 28 - Sept. 02, 2005 (a book from this school was published in 2007 with Kurt Sickafus and Blas Uberuaga as co-editors). Kurt Sickafus and Blas Uberuaga served as Guest Editors (NIM-B) for the proceedings of this conference. Blas is co-organizer of a symposium entitled "Materials Innovations for Next-Generation Nuclear Energy," which was held at the MRS Fall 2007 meeting in Boston, MA.

Interactions: Robin W. Grimes (Imperial College); Roger Smith (Loughborough University); Manabu Ishimaru (Osaka University); Kazuhiro Yasuda (Kyushu University); Simon Phillpot (U. Florida); Ivar Reimanis (Colo. School of Mines); Todd Allen (U. of Wisconsin); Brian Wirth (UC-Berkeley); Nigel Marks (U. Sydney). *Internal LANL Interactions*: Art Voter, Steve Valone, Marius Stan, Chris Stanek, Cynthia Reichhardt, Yongqiang Wang, Steve Conradson.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Ceramic Society to Frank Clinard (1986)
Foreign Distinguished Visiting Scientist at JAERI, Tokai, JAPAN to Frank Clinard (1987)
Los Alamos National Laboratory Fellow's Prize to Mike Nastasi (1995)
Fellow of the American Ceramic Society to Kurt Sickafus (1998)
Fellow of Los Alamos National Laboratory to Mike Nastasi (2000)
Los Alamos National Laboratory Fellow's Prize to Kurt Sickafus (2001)
2002 OBES Chunky Bullet competition co-winner (2002)

Personnel Commitments for FY2007 to Nearest +/-10%:
K. Sickafus (70%), J. Valdez (100%), B. Uberuaga (50%), M. Tang (50%), R. Greco (50%), I. Usov (25%).

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 809,000 **FY06 BA $** 1,026,000 **FY07 BA $** 793,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and possible subtask under FWP:
Multi-scale Study of the Role of Microstructure in the Deformation Behavior of Hexagonal Materials

FWP Number: SCPE401

Program Scope: Our goal is to use an integrated experimental and theoretical approach to characterize dislocation and twin structures in HCP, their interaction, and the role that they play during plastic deformation. The scope of the proposed work is to connect the various length scales and physical mechanisms governing deformation (micro, meso and macro scale), in order to explain the overall mechanical response of metallic aggregates. The focus of this program is hexagonal materials, where the basics of twinning transformation are not well understood, while they play a primary role in plasticity. The paradigm of this program is to reveal dislocation-twin coupling by studying complex testing histories involving changes in strain path, temperature, and strain rate

Major Program Achievements (over duration of support): This program uses polycrystal constitutive laws as a platform for implementing our understanding of microstructure into microstructure models, and relate them to macroscopic plastic response and anisotropy, for a wide range of strain, temperature and strain-rate regimes. We have developed **quantitative** experimental techniques for characterizing dislocation and twin structures in Zr and Mg (and to lesser extent to Be & Hf), and have incorporated such knowledge into our polycrystal models. Specifically, we have developed experiment-based models for dislocation walls, banding, primary and secondary twinning, and detwinning. We are making intensive and novel use of in-house neutron diffraction facilities for characterizing internal stresses and twinning. We started using the Advanced Photon Source (Argonne) for the same purpose. We have been able to characterize stress nucleation and associated stress relaxation. We have developed new automated EBSD analysis of twin fraction, and in-situ TEM observations of twin-dislocation reactions. We have developed new Multiple-State Embedded Atom Potentials for a basic understanding of dislocation-twin interactions in Zr. We have developed state-of-the-art physically-based polycrystal constitutive models for describing the mechanical response of HCP aggregates when subjected to complex loading histories.

Program impact: The effort on texture-, anisotropy-, and polycrystal-based constitutive descriptions of plasticity is relatively recent, changed the way in which the scientific community approaches constitutive modeling, and is the only viable approach to use in the case of HCP materials. Today the scientific community is going beyond the microscopy characterization of dislocations, grain boundaries and twins, and also aims to quantify the role that they play on the overall mechanical response of polycrystals. Such quest, which can only be answered through a basic and integrated study of such features, is the general scope of our program. And our team at Los Alamos is regarded as leading the field in such issues. We predict that our specific focus on hexagonal aggregates - Zr, Mg and Ti - will have a direct impact on basic material science, in Los Alamos research programs, and energy related technologies, such as nuclear, automotive and aeronautics. We foresee that a similar methodology can be applied and will impact the understanding of piezo-electric and shape-memory alloys where phase transformations are important.

Interactions: A. J. Beaudoin (U of IL-Urbana), I. Robertson (U. of IL-Urbana), D. Embury (McMaster U.), S. I. Wright (TexSEM Labs), J.P. Hirth (LANL consultant), S.R. Agnew (U. of Virginia), S. Kalidindi (Drexel U.), W. Horstemeyer (MS State U.), P. van Hove (Law. Berk. NL), R. Holt (Queen's U.), I. Karaman (Texas A&M U.), R. Asta (Northwestern U.), L. Toth (U of Metz, France)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP): U. Fred Kocks, Fellow, (NAE, TMS, LANL, ASM, APS, AIME); T.E. Mitchell, Fellow (LANL, TMS, ASM, APS, ACS), Honorary D. Sc., U. of Cambridge; Symp. and special issue of Phil. Mag. A in his honor; M.I. Baskes, Fellow (TMS, LANL, IP), DOE BES Award for Sustained Outstanding Research, Journal Editor, *Modeling and Sim. in Materials Sci. and Eng.*; About 20 Invited Presentations and about 30 papers published in International peer reviewed journals, in the last three years, related to this project.

Personnel Commitments for FY07 to Nearest +/- 10%: C. Tomé (PI, 50%), M. Baskes (5%), I. Beyerlein (40%), G Kaschner (30%), R. McCabe (25%), E. Cerreta (20%), B. Clausen (30%). POSTDOCS: G. Proust (100%), L. Capolungo (100%), D. Battacharya (50%), J. Wang (50%), C. Aydiner (30%), J. Neil (100%, PhD student).

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 1,001,000 **FY06 BA $** 981,000 **FY07 BA $** 981,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201030

FWP and possible subtask under FWP:
Nanophosphors: Fundamental Science of Insulators in the Nanoscale Regime

FWP Number:
SCPE972

Program Scope: Synthesis, and structural and luminescent characterization of nanophosphors (nanostructured inorganic, insulating luminescent materials) to assess the role of reduced dimensionality on their luminescent behavior, with particular focus on rare earth doped oxides. The localized nature of the electronic distribution of the rare earth ions make them excellent probes of changes in the local crystal field symmetry. Additionally, energy transfer phenomena can be probed through dopant concentration effects.

Major Program Achievements (over duration of support):

Nanophosphors have been produced by solution combustion synthesis. This is a robust technique that easily yields several grams of nanophosphors in the form of powders. It is based on exothermic redox reactions that undergo self-sustaining combustion. Mixtures of metal nitrates (oxidizers) and a fuel undergo spontaneous combustion under heating, and the chemical energy from the exothermic reaction heats the precursor mixture to high temperatures. The resulting ceramic foam is easily ground into a powder of macroscopic particles composed of a very large number of agglomerated nanocrystals with typical dimensions of tens of nm. Recently, we produced simple and complex oxide nanophosphors with emission intensities that rival bulk crystals. This is an unexpected result as luminescence efficiency is known to decrease with particle size due to the increasing contribution of surface quenching centers.

While electronic transitions in rare earth ions are highly localized and thus not expected to suffer quantum confinement effects, confinement effects can be manifested through changes of the phonon density of states. We obtained experimental evidence of this effect through heat capacity measurements of CeF_3 nanoparticles at low temperatures. Below ~4K, the heat capacity deviates from the expected T^3 law observed in all bulk materials, and freezes out suggesting the existence of a minimum phonon frequency in the density of states of the nanoparticles.

Long-lived phosphorescence, or afterglow, is a commonly observed, yet poorly understood luminescence phenomenon. Exposure of cerium doped yttrium and lutetium oxyorthosilicate single crystals to room lights for even a few minutes results in a blue afterglow (Ce^{3+} emission) that persists for more than a day. Significantly, we have prepared oxyorthosilicate nanophosphors that do not exhibit afterglow. Theoretical modeling of the temperature and dopant concentration dependence of the lifetime in oxyorthosilicate nanophosphors provided fundamental insights into energy transfer and radiative processes that span timescales from nanoseconds to seconds. The theoretical approach utilizes master rate equations to model the time evolution of energy (exciton) or charge (electron) transfer between donors (luminescent sites) and acceptors (traps and defects). By expanding the master rate equations to include back transfer from traps, we can account for the observed long lifetimes corresponding to afterglow. These findings were elucidated by electron paramagnetic resonance, thermally stimulated luminescence, photoluminescence and optical lifetime measurements on a comprehensive sample matrix prepared using a modified solution combustion synthesis technique.

Program impact: Evidence on unique luminescence behavior was obtained, including the role of structure, surface phenomena, and size effects. Energy transfer among rare earth dopants and the role of defects was investigated with a dual experimental-theoretical approach. In particular, structural disorder in oxyorthosilicate nanophosphors was experimentally characterized and related to luminescence behavior.

Interactions: P. A. Crozier (Arizona State Univ.), P. H. Holloway (University of Florida), Helmut Karl (Augsburg University, Germany) Internal LANL Interactions: A. Migliori, F. R. Trouw, Ernst I. Esch, K. Ott, R. Del Sesto, R. D. Gilbertson, E. McKigney, K. Sickafus, J. Valdez, B. Uberuaga, D. Smith, M. Graf, S. Conradson, M. P. Hehlen.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Invited talk at the Annual Solid State Meeting of the Brazilian Physical Society (May 2008)

Personnel Commitments for FY2007 to Nearest +/- 10%: R. Muenchausen (30%); L. Jacobsohn (20%); M. Blair (20%), B. Bennett (30%);.

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 450,000 **FY06 BA $** 441,000 **FY07 BA $** 350,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC02 01030

FWP and possible subtask under FWP:
Electronic Processes in Solid State Organic Electronic Materials
FWP Number:
SCPE973

Program Scope:
Organic electronic materials are condensed phases of conjugated organic molecules and intermolecular interactions are critical in determining the condensed phase properties. Because of the strong intermolecular interactions, the electronic properties of the dense films are not the same as those of the isolated molecules or single polymer chains. A major theme of this research is to determine which features of the electronic structure of the isolated molecules are maintained and which are modified in the condensed phase and to use our understanding of molecular electronic structure to describe the behavior of the condensed phases. The goal of the project is to provide an understanding of the fundamental physical processes that are important in determining the properties of organic electronic materials. Physical processes of particular interest include: electrical injection, charge transport, electron spin injection, transport and dynamics and exciton dynamics and transport.

Major Program Achievements (over duration of support):
Organic Spin Physics - Measured spin dependent magneto-optical properties of metal-organic compounds and developed a model based on Jahn-Teller distortion and the spin orbit interaction to describe the experimental results. Measured Schottky barrier energies for various ferromagnetic contacts to a series of organic semiconductors.
Electronic Structure of Condensed Phases of Organic Molecules – Used molecular dynamics calculations to determine solid state molecular configurations for PPV and PFO polymers. The molecular configurations were used as input to large scale quantum mechanical electronic structure calculations. The calculated electronic structure explains systematics observed in the transport and optical properties of these organic semiconductors.
Charge Transport in Composite Organic Semiconductors - Measured charge transport in isoelectronically doped organic semiconductors using time-of-flight transient photoconductivity and current-voltage characteristics of unipolar and bipolar test structures.
Organic Semiconductor Device Models - Developed the first device model for the light-emitting field effect transistor, recently invented at UC Santa Barbara and University of Cambridge. The model quantitatively describes the observed device properties.

Program impact:
Our integrated theoretical and experimental approach has demonstrated the important role of: spin orbit coupling in metal-organic systems; structural disorder in determining electrical transport properties of organic semiconductors; isoelectronic dopant energy levels in composite system charge transport; and carrier trapping at interfaces in organic field effect transistors.

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

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow American Association for the Advancement of Science (R. L. Martin); Co-Chair of Spring MRS Meeting on Solid State Lighting (B. Crone); Advisory Board of the Workshop on Spintronic Effects in Organic Semiconductors, Bologna 2007 (D. Smith); Organizing Committee 1st Topical Meeting on Spins in Organic Semiconductors, Salt Lake City 2009 (D. Smith).

Personnel Commitments for FY2007 to Nearest +/- 10%:
Ian Campbell: 20%; Brian Crone: 20%; Richard Martin: 20%; Darryl Smith: 30%

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $450,000 **FY06 BA $**441,000 **FY07 BA $** 441,000

Los Alamos National Laboratory
B&R Code: KC0201050

FWP and/or subtask Title under FWP:
Ion-Enhanced Synthesis of Materials
FWP Number:
SCPE407
Program Scope: To develop a fundamental understanding of ion and plasma processed materials and to determine how ion and plasma processing parameters influence the material structure and functional properties. Experiments, theory and modeling are used to understand the underlying physics and fundamental processes responsible for the enhanced properties derived by materials synthesis by these methods.
Major Program Achievements (over duration of support): We have successfully developed the Plasma Immersion Ion Process (PIIP) to synthesis diamond-like-carbon (DLC) field emitters. Modeling showed that electron emission is dependent sp^3 contents and the aspect ratio of the emitting area. PIIP was then used to alter the surface topology and ratio of sp^2 to sp^3 carbon bonding at the surface and thereby control the electron emission behavior.

We have shown that the intrinsic stress in thin films form by ion assisted deposition techniques are strongly influence by the presence of grain boundaries, vacancies, interstitials and dislocations. An atomic interaction model has been developed to explain the source of intrinsic stress in thin films.

We have developed a model that shows for the first time that the stress generated by radiation defects produced during the ion implantation of hydrogen into silicon promotes the formation of hydrogen-planner defects. The stress and resultant strain facilitate the nucleation and growth of hydrogen platelets on planes normal to the ion implantation direction

Using our model which describes the interaction between stress and hydrogen-defect complexes in Si, we have shown for the first time that it is possible accumulate hydrogen at discreet strain layers in Si and that the accumulation of hydrogen can lead to the fracture of a nm thick Si surface layer without the use of ion implantation.

Program impact: Provides fundamental insight at the microscopic and atomistic levels on how ion-solid interactions provide unique synthesis routes for the production of materials with enhance properties and functionalities. This work has enabled the synthesis of novel and improved materials.

Interactions:, J. Mayer (ASU), S. S. Lau (UCSD), P. Chu (City U, Hong Kong), D. Lucca (Oklahoma State), F. Rossi (JRC, Ispra Italy); *Internal LANL*: R. Hoagland, A. Misra, M. Baskes, J.G. Swadener, Q. Jia, J.K. Lee, L.G. Jacobsohn, D.W. Cooke

Recognitions, Honors and Awards: M. Nastasi: Fellow of APS (2006), Fellow of LANL (2000), Recipient LANL Fellows Prize (1995), R&D 100 Award (1997), Exec. Officer of The Bohmische Physical Society (1997-), Edit. Board of Nuclear Instruments and Methods in Physics Research, Section B: (1997-), Principal Ed. J. of Materials Research (1997-2000), Chair MRS Bull Pubs Subcommittee (1994-1999), Member of International Meeting Committees: Ion Beam Modification of Materials (1995-) , Ion Implantation Technology (2002-), Chair of the Editorial Board of MRS Bull (1996-1999), *Adjunct Professor*, Univ. of Colorado, Arizona State Univ., Univ. of Maryland. Contributions over the life of the program (1996 – present): ~ 220 papers; 3 books and 5 edited volumes;6 patents awarded; 4 PhDs awarded;

Personnel Commitments for FY2007 to Nearest +/- 10%: M. Nastasi (PI) 50%, Y. Wang (TSM) 10%, J.G Swadener (TSM) 10% L. Shao (postdoc) 50%,
Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 333,000 **FY06 BA $** 326,000 **FY07 BA $** 326,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202010

FWP and possible subtask under FWP:
Complex Electronic Materials

FWP Number: SCPE355

Program Scope: Research focuses on developing a fundamental understanding of the physics of complex and collective states in electronic materials by discovering new materials that reveal essential new physics. A necessarily broad range of experimental techniques, often at extremes of low temperatures, high fields and high pressures, is used to probe static and dynamic spin, charge and lattice degrees-of-freedom and their interactions on multiple length and time scales. Particular attention is given to highly correlated f-electron materials and layered cuprates, often in single crystal form, as exemplary complex electronic materials.

Major Program Achievements (over duration of support): Established the study of heavy-fermion materials as a new field of condensed matter physics through discoveries of numerous examples of unconventional superconducting, magnetic and semiconducting states in new correlated f-electron systems; discovered unconventional superconductivity in $PuCoGa_5$ and in a new family of Ce_nMIn_{3n+2} (M=Co, Rh, Ir; n=1,2) materials; discovered high T_c superconductivity in rare-earth cuprates, providing the first indication for the importance of CuO_2 planes; pioneered the now widely accepted importance of intrinsic inhomogeneity in the spin, charge and lattice of cuprates, using neutron and NMR spectroscopies; in $CeCoIn_5$, discovered evidence for Fulde-Ferrell-Larkin-Ovchinnikov state, first predicted nearly 40 years ago, and for an unusual form of quantum criticality; discovered superconductivity in hole-doped diamond; discovered a field-induced line of magnetic quantum-critical points within the pressure-induced superconducting state of $CeRhIn_5$.

Program Impact: Program is recognized internationally for its leadership in creating new science through the discovery and study of new correlated electron materials.

Interactions: Z. Fisk (U. C. Irvine), B. Buchner (Leibnitz Institute), P. Pagliuso (UNICAMP), J. M. Lawrence (U.C. Irvine), M. Nicklas and F. Steglich (Max-Planck Institute for the Chemical Physics of Solids), P. Oppeneer (Uppsala University), C. Booth (Lawrence Berkeley),V. Sidorov (IHPP, Troitsk), L. Greene (University of Illinois), A. Yazdani (Princeton), Q. Si (Rice University), C. Varma (U.C. Riverside), and D. Pines (U. C. Davis) among many others.

Recognitions, Honors and Awards (at least partially attributable to support under this FWP or subtask): Z. Fisk-National Academy of Science, American Academy of Arts and Sciences, E. O. Lawrence Prize, DOE Award for Sustained Outstanding Research in Solid State Physics, APS New Materials Prize, APS Fellow, APS Div. Condens. Matt. Phys. Executive Committee, APS Buckley Prize Committee, LANL Fellow, editorial boards of Physica B and Phys. Rev. Lett.; P. C. Hammel-APS Fellow, LANL Fellow, LANL Fellows' Prize, APS Executive Committee of Instrumentation and Measurement Science; R. H. Heffner-APS Fellow; R. Movshovich-APS Fellow, LANL Fellows' Prize, LANL Fellow; R. Pynn-APS Fellow, AAAS Fellow; J. L. Sarrao-APS Fellow, LANL Fellow's Prize; J. L. Smith- E. O. Lawrence Prize, DOE Award for Sustained Outstanding Research in Solid State Physics, APS New Materials Prize, APS Fellow, LANL Fellow, editorial boards of J. Alloys and Compds. and Phil. Mag.; J. D. Thompson- APS Fellow, AAAS Fellow, APS Div. Condens. Matt. Phys. Executive Committee, DOE Award for Sustained Outstanding Research in Solid State Physics, ISI Highly Cited Physicist, LANL Fellow, LANL Fellows' Prize, Japanese Society for the Promotion of Science Fellow; collectively served on numerous International Conference Advisory Committees and review panels, and within past year presented over 20 invited talks at international conferences/workshops/universities.

Personnel Commitments for FY2007 to Nearest +/-10%: J. D. Thompson (20%), W. Bao (20%), E. D. Bauer (20%), N. Curro (20%), R. Movshovich (20%), F. Ronning (20%); J. L. Sarrao (10%); three postdocs (50%)

Authorized Budget (BA) for FY05, FY06, FY07
FY05 BA $880,000 **FY06 BA** $850,000 **FY07 BA** $850,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202010

FWP and possible subtask under FWP:
FWP Complex Electronic Materials, subtask on Photoelectron Spectroscopy of Transuranics

FWP Number: SCPE355

Program Scope:
The electronic structure of actinides is investigated using photoelectron spectroscopy from a laser plasma light source (LPLS) as well as synchrotrons. The LPLS uses a laser, focused on a metal target to generate a plasma, emitting photons covering the actinide 5f resonance energies and the region of greatest change in the 5f and 6d cross-sections (27 to 140 eV). High resolution photoemission is carried out using a gas discharge lamp at fixed energies. The LPLS is the only tunable photon source dedicated to transuranic electronic structure studies. Surfaces are prepared by laser ablation allowing cleaning at low temperatures. Single crystal data has been acquired both on Pu compounds and isostructural Np and U compounds. The LPLS has produced photoemission data for ten Pu and Np compounds resulting in a much better understanding of the 5f electrons in bonding and hybridization. We have compound sequences involving U, Np and Pu. These sequences indicate localization effects in 5f actinides which are predictable and quantifiable in binding energy as well as temperature. Synchrotron results using angle-resolved photoemission (ARPES) yield insight into the narrow band behavior of families of actinides extensible to transuranic systems of interest. The successes in obtaining atomically clean Pu metal are now compared against Pu compound data which reveals a complex but reproducible signature for Pu 5f electron characteristics. In 2007 testing of the first angle-resolved photoemission system for Pu materials was completed. This APRES system will be dedicated to transuranic work early in 2008.

Major Program Achievements (over duration of support):
The program has over 50 publications and additionally two book chapters in the past 10 years with 40 of these publications emphasizing 5f material electronic structure. Published results include the first resonance photoemission data on Pu metal. Photoemission results for 10 transuranic compounds, Np metal and 2 phases of Pu metal. First photoemission measurements on the Pu superconductor $PuCoGa_5$ with mixed-level-model calculations in excellent agreement with the photoemission. Angle-resolved photoemission for USb_2 showing the narrowest 5f bands ever reported with a natural linewidth less than 5 meV and dispersion of 15 meV. Direct comparison between PES and calculations for α and δ-Pu. First measurement for Np compound hybridization and 5f bands. Demonstration of band behavior for actinide f-electrons. Design, construction, testing of the LPLS.

Program impact:
One of two programs world-wide to provide photoemission data on transuranic elements and compounds. Experimental results directly impact model calculations and the current thinking for transuranic materials. The only facility in the world with tunable photons for vacuum-ultra-violet or soft x-ray photoemission of transuranics.

Interactions:
External collaborators include G. Lander (Karlsruhe), C.G. Olson (Ames Lab), H. Hochst (Univ. of Wisconsin), P. Riseborough (Temple), O. Eriksson (Uppsala Univ), L. Havela (Charles University), M. Grioni (Lausanne), internal collaborators include L. Morales (MST-8), John Wills (T-1), Rich Martin (T-12) and David L. Clark (Seaborg Institute), Q. Jia (MPA-STC).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Los Alamos Distinguished Performance award for the LPLS project. Two Los Alamos Achievement Awards for LPLS work. Joyce elected to users advisory committee of Synchrotron Radiation Center (1999-present, chair 2003-2007), chair 36th SRC users meeting, co-chair MRS symposium on Actinides (2003), chair of LANL chemistry and materials science exploratory research committee (2006) .

Personnel Commitments for FY2007 to Nearest +/- 10%:
J.J. Joyce (30%), T. Durakiewicz (25%), K.S. Graham (10%)

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 300,000 **FY06 BA $** 300,000 **FY07 BA $** 300,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202010

FWP and possible subtask under FWP:
Control of structure-property relationships of complex oxide films by designed strain

FWP Number:
08SCPE355

Program Scope:
Development and application of neutron and X-ray (synchrotron) scattering techniques to elucidate the influence of strain on magnetic phase coexistence and texture in complex oxide films. Specifically, we will determine the parameters of the strain and magnetic free energies (e.g., stiffness, anisotropy, exchange, atomic and magnetic structure etc.) as a function of applied stress. This information will be used to test the theory of magnetic phase coexistence and texture in complex materials developed by Ahn et al. and to adapt their theory to explicitly treat magnetism.

Major Program Achievements (over duration of support):
I successfully defended this project as a new start April 2007. Capital equipment was acquired to upgrade our existing thin-film deposition system to deposit complex oxide films with large area (20 cm^2) suitable for neutron scattering. The equipment has been received and partially installed. I conducted a search for a postdoctoral researcher (for this project). **J. Olamit** accepted the offer and will start full-time work on this project in December 2007.

Program impact:
This project is a new project.

Interactions:
Discussed with **J. Budai (ORNL)** an opportunity to use microfocus synchrotron radiation to determine the atomic structures of ferromagnetic/conducting and antiferromagnetic/insulating phases in complex oxide films. Our intention is to undertake test measurements in the near future at the Advanced Photon Source.
Discussed with **J.K. Lee (LANL)** an opportunity to use ion implantation to bend substrates. This technique will allow us to apply a controlled tensile or compressive stress to the film (by bending its substrate). Lee successfully applied the technique to bend $SrTiO_3$—a candidate substrate for my study. I will characterize the strain of a few test samples in the near future.
Discussed with **T. Lookman (LANL)** his theory of strain and magnetic phase coexistence and texture in complex oxides. I understand what information Lookman requires, and how I will obtain this information with X-ray and neutron scattering.
Acquired two $La_{1/4}Pr_{3/8}Ca_{3/8}MnO_3$ (LPCMO) samples from **A. Biswas** (University of Florida, Gainesville). I measured the off specular reflectivity of the thicker sample using polarized neutron beams as a function of temperature and field.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Physical Society

Personnel Commitments for FY2007 to Nearest +/- 10%:
M.R. Fitzsimmons (30%)
Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $ 0 **FY06 BA $** 150,000 **FY07 BA $** 185,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202020

FWP and possible subtask under FWP:
Quantum Electronic Phenomena and Structures
FWP Number: SCPE395

Program Scope: This is a joint project between Sandia and Los Alamos National Laboratories, with Sandia leading the project. In an effort to focus our activities at LANL and couple better to the program at Sandia, we have decided to shift from research on energy transfer in nanophotonic materials, quantum dots, quantum wells and photonic crystal fibers to ultra-fast optical measurements in nanostructures including, e.g., 1D wires and Bloch oscillation devices, for the task of nanophotonics and ultra-fast optical studies in nanoelectronics. The shift reflects a better fit to the whole program. The goal of this project is the understanding of the behavior of quantum-based nanophotonic and nanoelectronic structures through the use of ultrafast optical techniques with the ability to separate their inherent complex many body interactions temporally. In detail, the three subtasks that form this project are to study (1) quantum transport in structured semiconductors, including electron-hole bilayers, 1D quantum wires, theoretical investigatation of exciton physics in nanoelectronics, and transport and quantum coherence in 2D quantum dot superlattices and heterostructures; (2) nanostructure synthesis and growth and their electrical and optical properties, and (3) nanophotonics and ultra-fast optical studies in nanoelectronics.

Major Program Achievements (over duration of support): A significant challenge for applications of "soft-matter" emitters based on, e.g., organic molecules or colloidal nanocrystals in optolelectronic devices is associated with difficulties in achieving electrical injection of charge carriers. Recently, we explored a novel approaches for injection of charges into semiconductor nanocrystals by using "noncontact" pumping mediated by high-efficiency energy transfer (ET) from a proximal quantum well (QW). To implement electronic injection,, we used an *inverted* LED design, in which an InGaN QW was grown on top of a thick, p-doped GaN barrier using metal-organic chemical-vapor deposition. The structure was further capped with a thin, 3-nm, n-type GaN layer and electrical contacts were applied by plasma etching. In this way it was possible to take advantage of the much higher mobility of n-GaN compared to p-GaN and to obtain significant current spreading despite the small thickness of the n-type injection layer. The structure was completed with a monolayer of CdSe nanocrystals, which was assembled on top of the n-type barrier. Using a micro-fluorescence system, we studied both spatial and spectral characteristics of electroluminescence from these hybrid structures and measured a color conversion efficiency of 15%. This value was much higher than the efficiencies expected for the traditional color-conversion scheme via absorption/re-emission, which clearly indicated the ET mechanism for excitation of the nanocrystals.

We have developed experimental tools and appropriate analytical and numerical models for studying complex nonlinear optical process in PCFs. For experimentally visualizing complex nonlinear optical processes in PCFs simultaneously in time-frequency we developed a unique Cross-Correlation Frequency-Resolved Optical Gating (XFROG) system which offers unprecedented resolution, sensitivity and bandwidth. An example of this technique is demonstrated through the remarkable behavior of the nanostructured waveguides is the supercontinuum (SC) generation by a propagating ultrashort optical pulse. Spectral-only measurements so far yielded only limited information and failed to help to completely explain the underlying nonlinear dynamics. We performed time-spectrally resolved measurements on SC formation and discovered unusual soliton dynamics in soft glass SF6 PCFs with pumping in the anomalous dispersion region at 1550 nm.

Program impact: This project addresses important scientific issues at the forefront of nanoscience. It complements ongoing R&D activities ongoing at the Center for Integrated Nanotechnologies.

Interactions: Department of Physics, University of Bath, UK; Department of Physics, University of Florida, Gainesville; Department of Chemistry, MIT; Department of Physics, Georgia State University, Department of Physics, Tufts University, Department of Physics, U. Massachusetts, Amherst

Recognitions, Honors and Awards: A.J. Taylor—Fellow of AAAS (2006); 15 invited talks; 13 publications; A.J. Taylor, Chair, OSA Nonlinear Optics Conference (2007), and Program Vice-Chair, GRC on Ultrafast Phenomena in Cooperative Systems (2006);

Personnel Commitments for FY2007: R. Prasankumar (TSM): 20%, D. Talbayev (postdoc), 75%

Authorized Budget (BA) for FY05, FY06, FY2007:

FY05 BA $ 190,000 **FY06 BA $** 140,000 **FY07 BA $** 140,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202020

FWP and/or subtask Title under FWP:
100 Tesla Science

FWP Number: SCPF100

Program Scope: The 15mm bore, 100T Multi-Shot (MS) at the NHMFL Los Alamos Pulsed Field Facility provides the highest magnetic fields in the world with 10ms duration. This unique environment enables the study of science in magnetic fields that for the first time approach higher temperature scales for interactions and smaller length scales than ever before, while the long duration of the pulse permits application of a broader spectrum of measurement techniques at higher precision, than the few microsecond destructive magnets that can achieve higher fields.

Major Program Achievements (over duration of support): In this, the first year of operation, successful 100 T experiments were published on dilute magnetic semiconductors, observation of the Shubnikov-de Haas effect in high T_c cuprate superconductors, dHvA studies of the high-field state of $CeIn_3$ and a measurement of an 81 T metamagnetic transition in an organic magnet. The 100T magnet was able, in each case, to reveal qualitative changes in behavior invisible at lower fields.

The difficult experimental environment in the 100T MS magnet has required the development of the "Digital Lock-In", an instrumentation package that is entirely NHMFL constructed and implements digital signal processing not available in any commercial instrument. It was tested at lower (60T, 10ms) fields on cuprate superconductors where new physics from Hall-effect measurements (the first in a short-pulse magnet) point toward universal behavior and a quantum critical regime. This resulted in two publications in Nature. Other techniques are on the way.

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 in alloys, 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.

Interactions: I. Bosovic, Brookhaven National Laboratory, Z. Fisk, UC Irvine, G.S. Boebinger, FSU, J. Musfeldt, UT, L Taillefer, U. Sherbrooke, N. Samanth, Penn. State

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow, Acoustical Soc. America-A. Migliori, Fellow, Los Alamos National Laboratory-J. Singleton, Fellow, APS-J. Singleton, LANL Fellows Prize-N. Harrison, APS Fellow-N. Harrison, AAAS Fellow-G. S Boebinger.

Personnel Commitments for FY2007 to Nearest +/-10%:A. Migliori, 30%, J.Singleton, 30%, J.B.Betts, 40%, N. Harrison, 40%, R. McDonald, 40%, Y. Suzuki (PD) 100%.

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 0 **FY06 BA $** 0 **FY07 BA $** 550,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202020

FWP and possible subtask under FWP:
Thermoacoustics for Hydrogen Production

FWP Number: SCPE979

Program Scope:
We focus on hydrogen-specific issues of thermoacoustic mixture separation. We consider which chemical reactions are most suitable for hydrogen production using thermoacoustics, and investigate scientific issues such as inter-channel thermoacoustic streaming, long-channel power transduction, and surface catalysis that will be important for use of thermoacoustics in this arena. We keep our general-purpose, publicly available thermoacoustics code DeltaE and its documentation aligned with the long-term vision of solar thermal hydrogen production.

Major Program Achievements (over duration of support):
We have thoroughly analyzed our original inspiration for this research, which was thermoacoustic separation of hydrogen and oxygen from thermally dissociated steam near 2600 Kelvin. We attempted a complete design of what might become a practical apparatus, to motivate our basic research by making note of the relevant gaps in our scientific and engineering knowledge. We concluded that this original inspiration is too challenging to be credible, and shifted our focus to the sulfur-iodine cycle. We revised our general-purpose, publicly available thermoacoustics code DeltaE to incorporate mixture-separation effects. We began designing a high-purity variation of thermoacoustic mixture separation that uses a very long, peristaltically driven separation tube.

Program Impact:

Interactions:
Penn State University; Qdrive.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

Personnel Commitments for FY2007 to Nearest +/- 10%:
Staff member G.W. Swift (20%), staff member D.A. Geller (0%), undergraduate J.P. Clark (40%)

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $0 **FY06 BA $**125,000 **FY07 BA $**125,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202030

FWP and/or subtask Title under FWP:
Accelerated Molecular Dynamics Methods

FWP Number: SCPE420

Program Scope:
The goals of this program are to develop methods for extending the time scale of molecular dynamics simulations to reach times relevant for diffusive processes and experiments; to improve the methods to make them applicable to the widest possible range of processes in chemistry, physics, materials science, nanotechnology, and biology; to apply the methods to problems of interest to LANL and DOE; and to collaborate with groups around the world to apply the methods to key problems in which they are expert.

Major Program Achievements (over duration of support):
Developed the parallel-replica dynamics method, which achieves parallel speedup for infrequent-event systems while maintaining exact dynamics. Developed the temperature accelerated dynamics (TAD) method, which achieves significant boost (many orders of magnitude) when barriers are high relative to the temperature. Used MD+TAD to simulate vapor-deposited metallic crystal and film growth at experimental deposition rates (seconds per monolayer), observing importance of highly concerted activated processes for surface smoothing even at low temperatures. Studied interstitial diffusion of H2 in fcc fullerene lattice, discovering unexpected multiple-occupancy mechanism. Performed first study of low-energy radiation damage and annealing on experimental time scales (seconds) with full atomistic detail (MgO). Developed modified parallel-replica dynamics method for driven systems. Achieved experimental strain rates in study of Cu grain boundary sliding.

Program impact:
The accelerated molecular dynamics 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 people view infrequent-event systems and activated processes. Accelerated molecular dynamics simulations 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.

Interactions:
LANL internal: ASCI Enhanced Surveillance program; Advanced Fuels (AFCI) program; BES ceramics radiation damage simulation program; DOE/OS SCIDAC program on stress corrosion cracking; LDRD program on extended length-scale accelerated dynamics. SCIDAC program on Stress Corrosion Cracking.
External: Jacques Amar (University of Toledo), Robert Carpick (Penn), Luciano Colombo (University of Cagliari, Italy), Jimmie Doll (Brown), John Harding (Universiy College London, UK), Robin Grimes (Imperial College, London), John Hamilton (Sandia National Laboratory, California), Graeme Henkelman (Texas), Hannes Jonsson (University of Iceland), Janna Maranas (Penn State), Ashlie Martini (Purue), Yuri Mishin (George Mason U.), Francesco Montalenti (University of Milano/Bicocca, Italy), David Sholl (Carnegie Mellon), Roger Smith (University of Loughborough, UK), James Sprague (Naval Research Laboratory), David Srolovitz (Princeton), Steve Stuart (Clemson), Greg Voth (Utah), Wolfgang Windl (Ohio State).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
A.F. Voter (PI):
Los Alamos Laboratory Fellow (2003)
Fellow of American Physical Society (2006)
Nominated to editorial boards of Journal of Chemical Physics and Theoretical Chemistry Accounts
Numerous invited talks at national and international conferences (e.g., ACS, APS, MRS, TMS, AIChE, E-MRS)

Personnel Commitments for FY2007 to Nearest +/- 10%:
A.F. Voter 50%; One postdoc; other postdocs and collaborators funded from other sources.

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 340,000 **FY06 BA $** 310,000 **FY07 BA $** 310,000

Laboratory Name: LANL
B&R Code: KC 0202030

FWP and possible subtask under FWP:
Integrated Modeling of Novel Materials

FWP Number:
SCPE420

Program Scope:
We have focused the theory effort to study short time and length scales to address electronic inhomogeneity at nanoscale and how these nanoscale effects modify properties of materials. We address features observed by state of the art probes of matter such as scanning tunneling microscopes (STM), time-resolved scanning tunneling microscopes, near field scanning optical microscopes (NSOM), and other local and fast probes will be developed and used. This work involves an attempt to understand the local and dynamical properties that are measured by these novel probes. We exploit these nanoscale features as a way to develop novel functionalities. Specifically, this work includes study of local electronic properties of strongly correlated materials and artificially created nanostructures, such as nanoscale dynamics of metal-insulator transitions, inhomogeneity in high-Tc and heavy fermion superconductors, impurity and vibronic states, Inelastic Electron Tunneling Spectroscopy (IETS), fast optical response of these materials, and electron-phonon coupled systems such as multiferroics. We will further develop numerical and analytic methods that will make possible detailed analysis and predictions about specific experimental properties.

Major Program Achievements (over duration of support):
Developed a microscopic theory of the STM detection of the bosonic collective modes in high-Tc materials. Developed a description of the dynamics of a dislocation glass as a possible explanation of supersolid behavior in 4He. Developed a microscopic description of the coupling between atomistic lattice distortions and the electronic properties of unconventional superconductors. Explained coupled charge-spin dynamics in multiferroic hexaferrites. Developed a theory of molecular electronic states in organic/inorganic hybrid structures. We have demonstrated the inhomogeneous nanoscale patterns that occur at the metal-insulator transition with novel correlated metal phase,

Program impact:
Applied advanced modeling and simulation tools to interpret and guide modern experimental probes of multiple spatial and temporal scales, including high magnetic fields, ultrafast time-resolved optical and vibrational spectroscopies, and scanning-tunneling microscopies.

Interactions:
Internal: J.D. Thompson, E. Bauer, T. Park (MPA-10) – heavy fermion Ce115 compounds, T Taylor, R. Averitt, R. Prasanumar(MPA-CINT), S. Crooker (NHMFL) – optics, S. Tretiak (T-12) – molecular electronics, Q. Jia(MST-STC) – multiferroics.
Several external collaborators: J.C. Davis (Cornell), E. Abrahams(Rutgers), T. Egami (Oak Ridge), P. C. Hammel (Ohio State), P. Littlewood (Cambridge), Allan H. MacDonald (UT Austin), Q. Si (Rice), L. Ku(Texas), J. Bonca and J. Demsar (Ljubliana), D. Basov(UCSD).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
A.V. Balatsky- LANL Lab Fellow, Oct 2005. International advisory committee, Spectroscopies of Novel Superconductors, 2005, 2007. APS March meeting 2007, Invited Talk; Ehrenfest Colloquium, Leiden University, Feb 2007.

Personnel Commitments for FY2007 to Nearest +/- 10%:
A.V. Balatsky – 25%
S.Trugman – 25%

Authorized Budget (BA) for FY05, FY07, FY2007:
FY05 BA $ 150,000 **FY06 BA $** 130,000 **FY07 BA $** 230,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Molecularly Engineered Biomimetic Nanoassemblies

FWP Number:
SCPE951

Program Scope:
The program aims to develop self-assembly and biologically-assisted assembly methods for the incorporation of selected optical and electronically active nanoscale components into assemblies and the development of materials that produce functions related to the control of electronic energy flow through assemblies. Relevant functions include photo-induced charge separation, directed electronic energy transfer, and manipulation of biological energetics and signaling processes. Focus on these functions and on use of a few active components is intended to also provide improved general understanding of structure and performance of the assembly types under study. The approach used includes materials synthesis and fabrication, static and time-resolved spectroscopies, optical and scanning probe microscopies, structural characterization, and modeling of electronic or optical responses.

Major Program Achievements (over duration of support):
Studied Langmuir-Blodgett assemblies of conjugated amphiphilic molecules that mediate photo-induced charge transfer between layers of conjugated polymers and LB-deposited amphiphilic fullerene derivatives, and of photoconductive thin films based on assembly of amphiphilic quaterthiophene derivatives. Studied the electronic and optical properties of amphiphilic organic and organometallic oligomers of conjugated phenylene acetylene compounds. Demonstrated that phospholipid bilayers and monolayers can be formed on electronically active surfaces of fullerenes and chemically modified fullerenes, and characterized the resulting assemblies using optical spectroscopy, microscopy, ellipsometry, and neutron reflectivity. Demonstrated the use of protein recognition strategies to form controlled multi-layer assemblies of phospholipids, characterized these assemblies using neutron reflectivity, ellipsometry, and atomic force microscopy, and showed that luminscent species can be incorporated into specific layers within the higher-order assemblies. Developed substrate-supported phospholipid membrane assemblies containing ion channels on active substrates to allow for optical measurement of ionic transport functions. Modulated the luminescence properties of water-soluble conjugated polymers through the use of polyelectrolyte interactions, and unraveled how heterogeneous assemblies in solution control the overall luminescent behavior. Developed water-soluble conjugated polymers with pH sensitive luminescence and absorption properties. Developed self-assembling colloidal charge-transfer assemblies of cationic conjugated polymers and anionic substituted fullerenes that demonstrate high efficiency photo-induced charge separation. Developed and characterized dendrimer and peptide templated luminscence metal nanoclusters formed in aqueous environments. Used Raman spectroscopy of surfactant-solubilized carbon nanotubes to provide quantitative determination of exciton-phonon coupling strengths.

Program impact:
The program has generated improved understanding of how to control complex self assembly to create functional nanoscale materials. Applications of such materials are found in energy production and storage, catalysis, and sensor technologies.

Interactions:
Atul N. Parikh (U.C. Davis); James A. Brozik (Washington State University); Darryl Sasaki (Sandia National Laboratories).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Invited presentations by key personnel (Shreve, Parikh, Wang, Sasaki and Martinez) at major national and international meetings.

Personnel Commitments for FY2007 to Nearest +/- 10%:
A. Shreve (20%); R. Rocha (20%); J. Martinez (10%); Y. Gao (postdoc, 50%); C. Wang (postdoc, 100%); H.-L. Wang (10%); S. Iyer (20%).

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $ 750,000 **FY06 BA** $ 600,000 **FY07 BA** $ 530,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Cooperative Phenomena in Molecular Nanocomposites.

FWP Number:
SCPE896

Program Scope:
The goal of this program is to create and study hybrid organic/inorganic materials in which cooperative self-assembly processes influence the formation and structure of the materials. This work includes the preparation of nanocomposite frameworks that are compatible with active biomolecular components, as determined by their structural integrity. Expertise in sample preparation and characterization is applied in an integrated manner to develop new insight into the balance between forces that govern the organization and responses of the materials studied. The program is performed collaboratively with researchers at Sandia National Laboratories.

Major Program Achievements (over duration of support):
Spectroscopic characterization of surfactant/silica mesophase nanocomposite films under controlled uv-light exposure. Masked deep-uv exposure has been used to remove the organic phase in self-assembled systems and organic/inorganic nanocomposite materials to generate patterned structure and organization in thin films as characterized by X-ray diffraction and various spectroscopic measurements. Developed methods for preparation and characterization of ordered nanocomposite silica films that can capture and spatially orient active proteins. Preparation of inorganic nanocomposite and nanoporous materials that contain molecular and macromolecular components to determine the effects incorporation of these components has on overall structure and assembly of nanostructured materials. Studied how nanostructure can affect the use of patterned nanocomposite materials for surface assisted mass spectrometry measurements. Prepared silica gel nanocomposites containing optically active carbon nanotubes.

Program impact:
This project has resulted in work published in high impact journals, such as *Nano letters*, *J. Phys. Chem. B*, and *Expert Reviews in Proteomics*. Developed a detailed understanding of organic template removal processes from organic/inorganic nanocomposite materials using photolytic methods. Development of spatially patterned biological/inorganic composite thin-film materials demonstrating increased stability and robustness of the biological components. Demonstrated that nanostructured materials deposited on silicon may be used to promote ionization/characterization of molecular compounds via a surface assisted mass spectrometry measurement.

Interactions:
Atul N. Parikh (U.C. Davis)
Alan Burns, Darryl Sasaki, Bruce Bunker, C. Jeff Brinker (Sandia National Laboratories, Albuquerque)
Andrew P. Shreve (Los Alamos National Laboratory)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Invited talk at Nanotech2007, La Jolla, CA; Asked to be a Nanotech2008 Technical Review Committee Member

Personnel Commitments for FY2007 to Nearest +/- 10%:
S. Chikkannanavar (10%)
J. Izraelevitz (100%)
J. Hanson (100%)
A. Dattelbaum (10%)

Authorized Budget (BA) for FY05, FY06, FY2007:
FY05 BA $ 85,000 **FY06 BA** $ 80,000 **FY07 BA** $ 80,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Fundamentals of Hydroxide Conducting Systems for Fuel Cells and Electrolyzers

FWP Number:
SCPE974

Program Scope:

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 combines experts in the area of fuel cells, synthetic chemistry and modeling to elucidate decay mechanisms and design new chemical structures to overcome them. Our focus is on fully characterizing cationic and developing advanced cations capable of being covalently tethered and having sufficient stability and conductivity for use in electrolysis or fuel cell applications. Physical processes of particular interest include: ion structure, ion charge distribution, interaction with water and anions, and the role of hydroxide versus carbonate.

Major Program Achievements (over duration of support):

Decay mechanisms of cations (including ammonium, sulfonium and phosphazenium) due to base attack have been identified under conditions relevant to fuel cells or electrolysis and accelerated conditions. While membranes based on 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 to much higher temperatures at sufficiently high water contents. The degradation of cations accelerates dramatically at low water contents (~5 waters per cation). The ability of water to stabilize cations to hydroxide attack has also been explored using molecular scale modeling. SN2 and ylide based decomposition routes have shown nearly equal activation barriers, and hydration studies of cations suggest water shields the cation from hydroxide in qualitative agreement with our chemical and thermal degradation studies. In particular our thermal degradation studies have shown isotopic exchange confirming the presence of ylide intermediates. Other tetraalkyl ammonium cations suggested from the literature to have increased stability have also been probed with those featuring an ether linkage showing the highest durability to date. The reasons for this increased stability are now the target of our computational studies as well as the study of other related cations.

Program impact:
The work has lead to the PI organizing an Army Research Office sponsored Alkaline Membrane Fuel Cell Workshop. Cation stability studies suggest the operating range of these materials can be expanded.

Interactions:
Organized ARO sponsored Workshop, involving 62 international attendees on Alkaline Membrane Fuel Cells. The program involves Electrochemical, Chemistry and Quantum Chemistry Groups at LANL.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
3 Invited talks at the Alkaline Membrane Fuel Cell Workshop held December 11-13, 2006, Phoenix, AZ.
Invited review article to Physical Chemistry Chemical Physics on the project topic.

Personnel Commitments for FY2007 to Nearest +/- 10%:
Bryan Pivovar: 20%; Shaji Chempath: 100%; Lawrence Pratt: 20%; James Boncella: 20%; Brian Einsla: 100%, Jacob Spendelow 10%, Clay Macomber 10%

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $ 400,000 **FY06 BA $** 400,000 **FY07 BA $** 400,000