

**Laboratory Name: LLNL**  
**B&R Code: KC020101**

**FWP and Possible Subtask under FWP:**

Observing Materials Dynamics on the Fundamental Atomic Scale by Ultrafast In-Situ TEM

**FWP number:**

SCW0754

**Program Scope:**

We aim to develop a fundamental understanding of materials dynamics (from microseconds to nanoseconds) in systems where the required combination of spatial and temporal resolution can only be reached by the dynamic transmission electron microscope (DTEM). In this regime, the DTEM is capable of studying nanoscale dynamic phenomena with several orders of magnitude time resolution advantage over any existing in-situ TEM, i.e. it is an ultra-fast atomic scale in-situ TEM. This capability is being used to develop new insights into active sites on nanoscale catalysts that are responsible for the selectivity of chemical reactions and the nucleation of nanostructures.

**Major Program Achievements (over duration of support):**

Initial specimen drive tests on the DTEM have shown that it is possible to nucleate and grow nanowires by laser ablation even without the presence of the gas flow – the mechanisms is slightly different from standard nanowire growth and suggests a high degree of flexibility in the control of nanowire structure and properties can be achieved in the DTEM. Preliminary tests on an in-situ stage have verified that it is possible to obtain a stable imaging condition (in a conventional 200kV TEM) even under gas flow conditions. In addition, tests on the DTEM have shown that the specimen drive laser can penetrate the windows of the environmental cell and provide localized sample heating – providing a clear indication that controlled catalytic reactions can now be performed in the DTEM. To support the experimental analyses of catalytic activity Molecular Dynamics (MD) simulations are underway. These calculations will determine the time scales achievable in an MD simulation using Density Functional Theory, leveraging existing access to LLNL's tera-scale computational facilities. Once these parameters have been set, we will be able to begin to use the *Metadynamics* rare events simulation technique to focus our efforts on specific reactions that occur on the long simulation time scales (nanoseconds) that correspond with the experiment.

**Program Impact:**

The demonstration of controlled environmental capabilities for the in-situ stage will allow *all* of the DTEM experiments being performed at LLNL to now utilize a controlled environment during the analysis. The ability to vary the environment around the sample means that the effect of the surface in the thin TEM sample on the dynamics of transitions can be investigated in a controlled manner. The demonstration of laser ablation inside of the DTEM shows that the microscope can be used as a functional instrument to drive nanotechnology in addition to being an instrument capable of characterizing nanostructures.

**Interactions:**

Professor B. C. Gates, UC-Davis – Nanoscale catalytic phenomena ; Professor W. A. Schroeder, UIC – Pulse compression for DTEM ; Professor J. C. H. Spence, ASU – Photofield emission tips for DTEM ; Dr. P. Stevens, ExxonMobil – Practical applications of in-situ stages for catalytic studies ; P. E. Fischione, Fischione Instruments – Development of an in-situ gas stage for catalytic studies

**Recognition, Honors and Awards:**

N. D. Browning program chair for *Frontiers of Electron Microscopy in Materials Science (FEMMS)*, Sonoma, CA, Sept 23-28, 2007

N. D. Browning invited presentation “Combining Spatial and Temporal Resolution in the Dynamic TEM”, *the 65th Annual Meeting of the Microscopical Society of America*, Ft Lauderdale, FL, August 5-9, 2007

N. D. Browning invited presentation “(S)TEM with high spatial, spectroscopic and temporal resolution”, UC-Berkeley, October 2007.

“In-Situ Laser Ablation Synthesis of Si Nanowires in the Dynamic TEM”, M.L. Taheri, B.W. Reed, T. Lagrange, & N. D. Browning, submitted *Nanoletters*

**Personnel Commitments for FY2008 to nearest +/- 10%:**

N. D. Browning (PI) - 50% ; N. Goldman (staff) – 25% ; J. B. Pesavento (staff) – 25% ; B. W. Reed (staff) – 25% ; M. L. Taheri (postdoc) – 75%

**Authorized Budget (BA) for FY05, FY06 and FY07:**

**FY05 BA \$0**

**FY06 BA \$0**

**FY07 BA \$650k**

**Laboratory Name:** Lawrence Livermore National Laboratory  
**B&R Code:** KC020101

**FWP and possible subtask under FWP:**

Complex Transient Events in Materials Studied Using Ultrafast Probes and Terascale Simulation

**FWP Number:** SCW0289

**Program Scope:**

We seek to study complex transient phenomena by applying ultrafast techniques to observe fundamental material processes that control properties. The new technique of dynamic transmission electron microscopy (DTEM) is a potentially powerful technique to characterize the evolution and identify mechanisms in fast, dynamic events in materials. We plan to explore the atomic level mechanisms and structures in martensitic transformations in materials, specifically the pressure driven  $\alpha$  to  $\epsilon$  transformation in Fe and the temperature driven  $\alpha$  to  $\beta$  transformation in Ti (and related systems, e.g. Zr, Hf). We are also studying phase nucleation and evolution in rapid solid-state chemical reactions in the reaction front of self-propagating reactive multilayer thin films.

**Major Program Achievements (over duration of support):**

We routinely operate the DTEM at LLNL in single shot mode with a 15 ns pulse of electrons containing  $1 \times 10^8$  electrons generated with a pulsed UV cathode laser. Transient states are initiated in the specimen by pumping it with a separate treatment laser. We have used specimen drive pulses of a few  $\mu\text{J}$  to heat specimens of Ti into the  $\beta$  phase field and quantified their structural transformation as a function of time with selected area electron diffraction. We have used these data to construct the first isothermal time-temperature-transformation (TTT) diagram with nanosecond time resolution. Fitting these data to analytical models of martensite nucleation and growth to calculate a temperature dependent activation energy for the transformation has revealed the importance of autonucleation in the low temperature regimes of the transformation and may account for the observed, rapid transformation rates. We have also identified a transient cellular growth morphology at the reaction front in reactive multilayer thin films.

**Program impact:**

We have commissioned an instrument that can perform electron diffraction and imaging with high spatial resolution of better than 10 nm and on the time scale of 15 ns. This is the highest combination of spatial and temporal resolution ever achieved with any characterization technique. We have also reached out to the academic community, forming collaborations with several institutions (see below) on high impact areas of study.

**Interactions:**

Internal—High Performance Computational Materials Science and Chemistry Group, Nanoscale Materials Science and Technology Group, Metallurgy Group, Ultrafast Materials Science Group, National Ignition Facility, H-Division (Condensed Matter Physics), Center for Applied Computer Science

External—Argonne National Laboratory, Lawrence Berkeley National Laboratory, Oak Ridge National Laboratory, Sandia National Laboratory, Purdue University, Michigan State University, University of Illinois, Chicago, University of Illinois, Urbana-Champaign, Arizona State University, University of Pittsburgh, University of California, Davis, University of California, Los Angeles, Technical University, Berlin, Max Planck Institute, Stuttgart

**Recognitions, Honors and Awards (partly attributable to support under this FWP or subtask):**

G.H. Campbell—Editorial Board (Key Reader) Metallurgical and Materials Transactions A. Invited presentations at M&M 2006, Gordon Research Conference on Physical Metallurgy 2006, MRS Fall Meeting 2006, European Microscopy Conference 2008.

T.B. LaGrange—Winner of Best Poster at Post Doc Symposium held at LLNL 2006. Invited presentations at Frontiers of Electron Microscopy in Materials Science 2007, at Lawrence Berkeley National Laboratory on Advanced Techniques and Technologies for Electron Microscopy 2007, and a workshop held at Lawrence Berkeley National Laboratory on *In Situ* Techniques for Nanomechanics 2007.

J.S. Kim—Student attendee at the Annual Meeting of Nobel Laureates, Lindau 2006, Graduate Student Travel Award for the International Microscopy Conference, Sapporo 2006.

**Personnel Commitments for FY2008 to Nearest +/- 10%:**

Dr. G.H. Campbell (PI) (30%), Dr. T.B. Lagrange (staff) (80%), Ms. J.S. Kim (student) (100% time on this project, however her effort is supported by a LLNL SEGRF scholarship).

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

**FY05 BA \$359k**

**FY06 BA \$352k**

**FY07 BA \$352k**

**Laboratory Name:** Lawrence Livermore National Lab.  
**B&R Code:** KC020102

**FWP and possible subtask under FWP:**

Microstructural evolution and mechanical response of complex alloys under prolonged particle radiation

**FWP Number:** SCW0343

**Program Scope:**

Development of new quantitative methods for simulations of microstructure evolution in irradiated materials. New algorithms for microstructure simulations reaching length and time scales typical of material working life in real reactors. This research effort is motivated by the acute need and an emerging possibility to use material simulations to enhance reliability of material tests in the new experimental testing facilities being developed within the international R&D programs on fission and fusion reactors.

**Major Program Achievements (over duration of support):**

*Real-space microstructure simulator:* Developed a new kernel-free implementation of the Fast Multipole method for fast updates of elastic strain fields in the evolving material microstructure. Implemented the new method in an efficient computer code suitable for microstructure simulations.

*First-passage Monte Carlo:* Adapted the new first-passage Monte Carlo algorithm for simulations of microstructure evolution in iron and iron-based alloys subjected to electron and particle irradiation. The new method extends the time horizon of Monte Carlo simulations of material microstructure from hours and days to tens and hundreds of years.

**Program Impact:**

The new method of first-passage Monte Carlo overcomes the severe computational limitations of the accurate microstructure simulations making it possible to model material degradation under the dose rates and up to total damage doses typical of the existing and future fission and fusion reactors. This constitutes a major breakthrough in microstructure simulation capabilities and should have a significant impact on several national and international programs focused on materials for nuclear energy applications.

**Interactions:**

LLNL (M. Kalos, B. Sadigh)  
UIUC (R. Averback, P. Bellon and I. Robertson)  
Stanford University (W. Cai, D. Barnett)  
CEA Saclay, France (F. Willaime, M. Nastar)  
UKAEA and Oxford University, UK (S. Dudarev, S. Fitzgerald)  
Queen's University Belfast, UK (A. Paxton)

**Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):**

6 invited talks by V. Bulatov, G. Gilmer and A. Donev.  
T. Opplestrup, V. V. Bulatov, G. H. Gilmer *et al.* First-passage Monte Carlo algorithm: diffusion without all the hops, *Phys. Rev. Lett.* **97**, 230602 (2006).

**Personnel Commitments for FY2007 to Nearest +/-10%:**

V. Bulatov (30%)  
G. Gilmer (30%)  
Graduate student T. Oppelstrup (25%)  
Lawrence postdoc A. Donev (10%)

**Authorized Budget (BA) for FY06, FY07:**

**FY06 BA** \$360,000

**FY07 BA** \$294

**Laboratory Name: LLNL**  
**B&R Code: KC020203**

**FWP and possible subtask under FWP:**

Understanding Molecular Hydrogen Absorbents: A First Principles Theory for van der Waals Interactions  
**FWP Number: SCW0289**

**Program Scope:**

This project is focused on the development of efficient methods for using first-principles calculations to accurately predict weak interactions in materials. We are developing modifications to the widely used local density functional theory to explicitly include non-local correlation effects particularly tailored for van der Waals (vdW) interactions. In implementing our approach, we are using linear scaling quantum Monte Carlo (QMC) methods to develop a database for vdW interactions between molecular hydrogen and various materials. These methods are applicable to a wide range of systems whose properties depend on weak interactions, such as vdW solids or biological molecules. However, our primary focus is on examining materials for storing molecular hydrogen via physisorption onto surfaces. These calculations will be used to evaluate candidate materials for storing hydrogen for use on fuel cell powered vehicles.

**Major Program Achievements (over duration of support):**

Our initial studies of the adsorption of molecular hydrogen on boron doped fullerenes demonstrated promise for the QMC method as a route to obtaining benchmark grade binding energies for systems of relevance to hydrogen storage. We have continued to develop our understanding of and ability to control the systematic errors inherent in the fixed node approximation as applied to these systems and have now performed a systematic study of a wide variety of closed shell systems with dispersive interactions within the fixed-node QMC ansatz. Systems studied to date include the argon dimer, trimer, tetramer and bulk argon as well as the benzene dimer and hydrogen interacting with benzene, coronene and graphene sheets. We have found that the fixed node error with a single determinant wavefunction defining the nodal surface can be several orders of magnitude larger than the binding energy in these challenging systems. Nevertheless, judicious application of a more general variational ansatz (backflow in particular) and the development of advanced optimization techniques have allowed us to successfully resolve the binding energies for these systems to within a few MeV. This represents an order of magnitude increase in accuracy over previous applications of QMC to these systems.

**Program impact:**

The methods we are developing in the project will have a broad impact in computational materials science. Specifically, this work will enable more accurate and efficient calculations on a wide range of materials, including biologically relevant systems and hydrogen storage materials. The specific application area of physisorption of hydrogen storage materials will help to establish the scientific base for the DOE/EERE go/no go decision on the use of molecular absorbents by FY09.

**Interactions:**

National Renewable Energy Laboratory (Dr. Shengbai Zhang, Dr. Yong-Hyun Kim)  
LLNL (Dr. Randolph Q. Hood)  
Cornell University (Prof. Cyrus Umrigar)  
University of California, Berkeley (Dr. Jeffrey C. Grossman, Dr. Lucas Wagner)  
Northwestern University (Norman Tubman, 2007 CCMS summer student)

**Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):**

Invited talk for Dr. J. DuBois at the 2008 Spring MRS meeting "Quantum Monte Carlo benchmarks for dispersive interactions". Invited talk for Dr. S. Hamel at the 2008 Spring MRS meeting "First-principles simulations of non-covalent interactions". Invited talk for Dr. J. DuBois at the 2008 EERE/BES workshop "Theory Focus Session on Hydrogen Storage Materials".

**Personnel Commitments for FY2007 to Nearest +/- 10%:**

Dr. Eric Schweigler (10%), Dr. Jonathan DuBois (75%), Dr. Sebastien Hamel (10%)

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

**FY06 BA \$150k**

**FY07 BA \$150k**

**FY08 BA \$150k**

**Laboratory Name: LLNL**  
**B&R Code: KC020203**

**FWP and possible subtask under FWP:**

Ab initio Design of Nanomaterials with Pressure: The Search for Novel Materials

**FWP Number:** SCW0289

**Program Scope:**

In this program, we are using first-principles electronic structure simulations to investigate the use of pressure to control the properties of materials at the nanoscale. We are combining our recently developed capabilities for modeling nanoscale materials and materials under pressure to examine nanoscale materials under pressure, composite nanomaterials with built-in pressure, and the phase diagrams of nanoparticle arrays. These simulations will be used to explore new properties and structural phases of nanomaterials, which can be accessed by applying pressure and in some cases locked-in by constructing composite nanomaterials. Through this systematic process, we will separately engineer nanomaterials building blocks with novel, pressure-induced properties, and design the composite nanomaterials with technologically desirable material properties.

**Major Program Achievements (over duration of support):**

In collaboration with an experimental DAC team at LLNL, we have carried out an extensive study of the optical properties of CdSe nanoparticles under pressure. Our theoretical calculations provided conclusive evidence that the observed anomalous photoluminescence behavior is due to non-hydrostatic stresses. A manuscript describing this work is currently under review in the journal *Small*. We have completed a number of algorithmic developments: first-ever implementation of a DFT enthalpy functional approach in PWscf for continuum pressure mediums, a hybrid QM/MM approach in Qbox for atomistic pressure mediums, a web-based tool StrainBands for examining semiconductors under pressure.

**Program impact:**

This systematic theoretical exploration of pressure, in connection with experiments carried out both at LLNL and ORNL, promises to unveil both new materials and novel basic physical properties of materials at the nanoscale.

**Interactions:**

Oak Ridge National Laboratory (Dr. Fernando Reboredo, Dr. Murilo Tiago)

Massachusetts Institute of Technology (Prof. Nicola Mazari)

Boston University (Prof. Luca dal Negro)

University of California, Berkeley (Dr. Jeffrey Grossman, Dr. Yosuke Kanai)

LLNL (Dr. Natalia Zaitseva, Dr. Christian D. Grant, Dr. Jonathan Crowhurst, Dr. Erik Draeger)

**Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):**

L. Dal Negro, J.H. Yi, M. Hiltunen, J. Michel, L.C. Kimerling, S. Hamel, A. Williamson, G. Galli, T.F. Chang, V. Sukhovatkin and E.H. Sargent, "Light-emitting silicon nitride systems and photonic structures," *J. Exp. Nanoscience*, 1(1) 29-50 (2006); L. Dal Negro, Jae Hyung Yi, Lionel C. Kimerling, Sebastien Hamel, Andrew Williamson and Giulia Galli, "Light-Emitting Silicon Nanocrystals and Photonic Structures in Silicon Nitride", *IEEE J. Select. Topics Quantum Electron.* 12(6) 1628-1635 (2006); N. Zaitseva, S. Hamel, Z. Dai, C. Saw, A. Williamson, G. Galli, "Effect of nitrogen on the stability of Si nanocrystals formed by decomposition of alkyl silanes", submitted to *J. Phys. Chem. C* (2007); C. D. Grant, J. C. Crowhurst, S. Hamel, A. Williamson, N. Zaitseva, "Anomalous photoluminescence in CdSe quantum dot solids at high pressure due to non-uniform stress", submitted to *Small* (2007); L. Dal Negro, R. Li, J. Warga, S. Yerci, S.N. Basu, S. Hamel, and G. Galli, *Light Emission from Silicon-Rich Nitride Nanostructures, in Silicon Nanophotonics: Basic principles, Present Status and Perspectives*, edited by L. Khriachtchev, Pan Stanford Publishing, 2008.

**Personnel Commitments for FY2007 to Nearest +/- 10%:**

Dr. Eric Schwegler (10%), Dr. Tadashi Ogitsu (10%), Dr. Heather Whitley (75%), Dr. Sebastien Hamel (10%), Dr. Byeongchan Lee (20%)

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

**FY06 BA \$350k**

**FY07 BA \$350k**

**FY08 BA \$350k**

**Laboratory Name:** Lawrence Livermore National Laboratory  
**B&R Code:** KC020301

**FWP and possible subtask under FWP:**

Virus assembly at nanoscale chemical templates

**FWP Number:** SCW0289

**Program Scope:**

The purpose of this research is to use templated deposition of engineered viruses as a way of investigating the physics that controls directed organization of complex biomolecules at surfaces. Site-specific engineering of viral proteins, synthesis of chemoselective linker molecules, and nanoscale patterning of those linkers will be used to create the viral arrays. Chemical force, confocal, and atomic force microscopy will be employed to characterize virus-virus and virus-substrate interactions, the kinetics of early aggregation events, and the morphology of assembly, respectively. Molecular dynamics and kinetic Monte Carlo simulations will be compared to the experimental results in order to build a physical picture of the aggregation and assembly process. This research is motivated by the potential of viruses arrays as vehicles for creating predefined micron-scale patterns of functional molecules and materials which are in turn organized at the molecular level by the viral template.

**Major Program Achievements (over duration of support):**

Used force spectroscopy to measure virus-virus and virus template binding forces and extract binding enthalpies. Established new force spectroscopy-based methodology for direct measurement of free energies of binding. Created kinetic Monte Carlo routine to predict morphology of virus arrays at chemical templates that predict similar morphologies to those observed in experiments. Developed set of chemical linkers that selectively bind tobacco mosaic virus protein (TMVp) disks at templates. Introduced dual modifications to TMVp to give simultaneous surface immobilization and fluorescence. Developed model system for investigating evolution of organic and inorganic components during templated crystallization.

**Program Impact:** Has resulted in collaboration between interdisciplinary group of biologists, chemists, physicists and materials scientists at three major universities and multiple groups within the Biosecurity and Nanosciences Laboratory at LLNL. Has produced the first suite of experimental and theoretical results that go reveal underlying physical principles controlling virus organization at chemical templates.

**Interactions:**

Internal—Computational Materials Sciences Group; Molecular imaging, Nanophotonics, and Molecular biophysics and functional nanostructures Groups within the Biosecurity and Nanosciences Laboratory, LLNL  
External—Department of Materials Science and Engineering and Department of Biological Engineering, Massachusetts Institute of Technology; Department of Molecular Biology, The Scripps Research Institute; Department of Chemistry, University of California at Berkeley.

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

J.J. De Yoreo – Fellow of the American Physical Society; Associate Editor for Journal of Crystal Growth; Co-Chair and co-organizer of the 13<sup>th</sup> International Summer School on Crystal Growth; Plenary speaker (on biocrystallization and biologically directed assembly) at the 15<sup>th</sup> International Conference on Crystal Growth and Epitaxy; Chair for the 2008 Gordon Conference on Biomineralization

**Personnel Commitments for FY2007 to Nearest +/- 10%:**

A. Noy (20%); J. De Yoreo (10%); G. Gilmer (20%); A. Presley (100%); R. Friddle (80%); S. Elhadj (50%); A. Belcher (8%); R. Barbero (50%); M. Estrada (50%).

**Authorized Budget (BA) for FY03, FY04, FY2005:**

**FY05 BA \$0**

**FY06 BA \$459**

**FY07 BA \$459**

**Laboratory Name: Lawrence Livermore National Lab**  
**B&R Code: KC020301**

**FWP/subtask Title under FWP:** Investigations of Electron Correlation in Complex Systems

**FWP Number:** SCW0289

**Principal Investigator:** Jim Tobin

**Program Scope:** We are developing and utilizing photon dichroic and spin resolved techniques to investigate electron correlation in complex systems. These materials include potential spintronic device sources such as the proposed half-metallic ferromagnetic Fe<sub>3</sub>O<sub>4</sub> and f electronic materials such as non-magnetic Ce and  $\delta$ -Pu.

**Major Program Achievements:**

Using Ce, we have experimentally confirmed the underlying assumption of all Kondo-like models: the antiparallel alignment of the lower Hubbard band and quasiparticle (Kondo) peak. We have further tested the validity of Fano Spectroscopy using Pt as a surrogate system for Pu: Pt is a large spin-orbit, partially filled, highly relativistic 5d system and it exhibits a large Fano Effect.

**Refereed Journal Publications in calendar year 2007 (also 4 more Conference Proceedings):**

1. J.G. Tobin, S.W. Yu, T. Komesu, B.W. Chung, S.A. Morton, and G.D. Waddill, "Evidence of Dynamical Spin Shielding in Ce from Spin-resolved Photoelectron Spectroscopy," *EuroPhysics Letters* **77**, 17004 (2007).
2. J.G. Tobin, S.A. Morton, S.W. Yu, G.D. Waddill, I.K. Schuller, and S.A. Chambers, "Spin-Resolved Photoelectron Spectroscopy of Fe<sub>3</sub>O<sub>4</sub>: the case against half-metallicity," *J. Phys. Condens. Matter* **19**, 315218 (2007).
3. J.G. Tobin, "Beyond Spin-Orbit: Probing Electron Correlation in the Pu 5f States," *J. Alloys Cmpds* **444-445**, 154 (2007).
4. T. Komesu, G.D. Waddill, S.W. Yu and J.G. Tobin, "Spin dependent electron transmission through ferromagnetic thin films," *Physics Letters A* **368**, 129 (2007).
5. J.G. Tobin, S.A. Morton, S.W. Yu, T. Komesu, G.D. Waddill and P.A. Boyd, "Spin Spectrometer at the ALS and APS," *Nucl. Instrum. Methods A* **582**, 162 (2007).
6. G.J. Mankey, S.A. Morton, J.G. Tobin, and S.W. Yu, and G.D. Waddill, "A spin- and angle-resolved photoelectron spectrometer," *Nucl. Instrum. Methods A* **582**, 165 (2007).
7. S.W. Yu and J.G. Tobin, "Observation of the underlying relativistic effect in the valence bands of Pt," *Surface Science Letters*, 2007, in press (doi:10.1016/j.susc.2007.07.034).

**Invited Talks in calendar year 2007:**

1. J.G. Tobin, "Observation of Dynamical Spin Shielding in Ce: Why It Matters for Pu Electronic Structure," 37<sup>th</sup> Journées des Actinides Conference, Sesimbra, Portugal, March 24-27, 2007.
2. J.G. Tobin, "Observation of Dynamical Spin Shielding in Ce: Why It Matters for Pu Electronic Structure," JOWOG32MAT, LANL, Los Alamos, NM, June 18-22, 2007.
3. J.G. Tobin, "Observation of Dynamical Spin Shielding in Ce: Why It Matters for Pu Electronic Structure," Workshop on the Fundamental Properties of Plutonium, VNIIEF, Sarov, Nizhny Novgorod Region, Russia, June 25 -29, 2007.

**Program Impact:**

We are pursuing Double Polarization Photoelectron Dichroism measurements of the Fano Effect, using spin resolving detection in photoelectron spectroscopy, to test the nature of electron correlation in Pu. (See Publication 3.) If successful, we will solve the riddle of Pu electronic structure that has remained unresolved for the last 60 years. We have successfully tested this technique on Ce, the 4f analog of Pu, and the 5d surrogate system Pt. (See Publications 1 and 7.) We are also developing a Bremsstrahlung Isochromat Spectroscopy (BIS) capability to permit the direct measurement of the unoccupied electronic structure of Pu, which is another missing piece in the puzzle of Pu electronic structure.

**Interactions:**

Collaborators - USA- National Labs: LBNL- S.A. Morton; PNNL-S.A. Chambers; USA-Universities: UMR-G.D. Waddill, T. Komesu; UCSD- I.K. Schuller; UA- G.J. Mankey. Both the APS at Argonne National Laboratory and the ALS at Lawrence Berkeley National Laboratory have been used for this work. We interact frequently with the personnel from LANL. (See Invited Talks #2 and #3 for examples.)

**Personnel Commitments for FY2007:**

JG Tobin 50%, Sung Woo Yu 50%

**Authorized Budget (BA) for FY06, FY07, FY08:**

**FY05 BA \$300,000**

**FY06 BA \$300,000**

**FY07 BA \$300,000**



**Laboratory Name:** Lawrence Livermore  
**B&R Code:** KC020301

**FWP and/or subtask Title under FWP:**

Manipulation and Quantitative Interrogation of Nanostructures

**FWP Number:** SCW0289

**Program Scope:**

The goal of this project is the characterization of the surface, geometric and electronic structure of nanostructured material. We employ unique methods of particle synthesis that allow the greatest control over these physical parameters and utilize state-of-the-art synchrotron radiation-based characterization methods that provide element-specific atomic and electronic structure information. This powerful combination has proven most valuable to the condensed matter theory community who have compared the experimental data to their computation results with and, as a direct result, helped refine our understanding of quantum dot structure/property relationships and guided new material discovery.

**Major Program Achievements (over duration of support):**

Diamondoids, hydrocarbon molecules with cubic-diamond-cage structures, have unique properties with potential value for various nanotechnology applications. The ability to functionalize this special class of nanodiamond materials opens new possibilities for surface-modification, high-efficiency field emitters in molecular electronics, as seed crystals for diamond growth, or as robust mechanical coatings. We have examined the effects of thiol substitution position and polymantane order on diamondoid monolayers on gold using near-edge x-ray absorption fine structure spectroscopy (NEXAFS) and x-ray photoelectron spectroscopy (XPS). Control over the orientation of diamondoid monolayers using selectively thiolated diamondoids adamantane, diamantane, triamantane, and [121]tetramantane on gold has been demonstrated. We also found monochromatic electron photoemission from large-area self-assembled monolayers (SAM) of a functionalized diamondoid, [121]tetramantane-6-thiol. Photoelectron spectra of the diamondoid monolayers exhibited a peak at the low-kinetic energy threshold; up to 68% of all emitted electrons were emitted within this single energy peak. The intensity of the emission peak is indicative of diamondoids being negative electron affinity materials. With an energy distribution width of less than 0.5 electron volts, this source of monochromatic electrons may find application in technologies such as electron microscopy, electron beam lithography, and field-emission flat-panel displays.

**Program Impact:**

We have measured the electronic and geometric structure of ordered arrays of thiolated diamond nanoparticles. These diamondoid monolayers show a unique monochromatic electron photoemission which is indicative of being a negative electron affinity (NEA) material. NEA in this class of nanomaterials has significant technological implications.

**Interactions:**

Internal: J. De Yoero, CMELS Directorate, J.E. Klepeis, Physics and Advanced Technology Directorate LLNL.  
External: Stanford- Z.X. Shen, N. Melosh; UC Santa Cruz- J. Zhang; UC Davis- S. Risbud; Molecular Diamond Technologies, Chevron Technology Ventures- B. Carlson, J. Dahl; University of Giessen- P.R. Schreiner; USN Research Laboratory- H. Mattoussi.

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

TvB- member of Advanced Light Source (ALS) Science Advisory Committee, Meeting Chair of the combined 2007 ALS Molecular Foundry Users meeting, Chair elect of the 2007 ALS users executive. The group has given six invited talks at international and national meetings on work supported by this BES project

**Personnel Commitments for FY2004 to Nearest +/- 10%:**

T. van Buuren (staff scientist) 5% T. Willey (staff scientist) 20% Jon Lee (post-doc) 33% Rob Meulenberg (staff scientist) (10%), April Monotyva Vaverka (student) 100% on this project but paid only 20% by DOE.

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

**FY05: BA** \$300,000

**FY06 BA:** \$300,000

**FY07 BA:** \$300,000