Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020101

FWP and possible subtask under FWP: Structure and Phase Transformations of Nanophases Embedded in Solids
FWP Number: KC11A

Program Scope: This program investigates the structure and behavior of embedded nanophases. On the fundamental research side, we explore the effect of embedding parameters such as crystallographic and elastic constraints on the behavior of inclusions. On the applied side, we utilize these parameters to manipulate microstructures and improve materials properties. Concepts employed in this work include the use of crystalline symmetry as an alignment field for nanoscale inclusions, solid state wetting to control the topology of two-phase microstructures, or differential kinetics and thermodynamics to manage precipitate distributions. The unique capacity of advanced electron microscopy to probe individual nanoparticles embedded inside a solid matrix leverages the advanced instrumentation available at NCEM. Our approach covers an aspect of nanoscience that will become increasingly important as nanoparticles are being made into macroscopic materials by consolidating or embedding them in a solid. In the long term, the concepts developed under this program will provide essential tools for the engineering and design of nanoscale materials.

Major Program Achievements (over duration of support):

We have developed a new approach to producing monodisperse core/shell inclusions in a solid matrix via simple solid-state reactions. Using spinodal decomposition to generate a transient array of heterogeneous nucleation sites, a uniform distribution of small particles with a Sc-rich core surrounded by a Li-rich shell a few nanometers thick can be made. This approach of employing kinetic and thermodynamic parameters to generate precipitate distributions can be applied to a range of alloys and could lead to new types of dispersion-strengthened materials.

By combining high resolution electron microscopy with 3D atom probe data, we have been able to confirm directly the hypothesis of pre-precipitation clustering driven by strain compensation. The electron microscopy data showed that clusters had not yet transformed to the diamond cubic structure of precipitates while the atom probe proved that clusters contained both Si and Ge. Similar clusters were absent in binary alloys.

We have synthesized nanocomposite alloy films of Al-Mo far from equilibrium by using room temperature co-sputtering. A systematic investigation of microstructure and properties as a function of Mo content resulted in an optimum film composition of Al-32at%Mo with a unique microstructure comprised of a dense distribution of nanometer-scale Mo crystallites dispersed in an amorphous Al-rich matrix. These films make ideal materials for NEMS device applications. Based on data from detailed characterization, it was possible to predict the evolution of these unusual microstructures using thermodynamic and kinetic modeling.

Program Impact:
This work has led to an improved understanding of the key role played by embedding parameters in the evolution of microstructures. In particular, the role of crystallographic alignment and confinement in a solid matrix on the behavior of nanoscale particles has been elucidated and utilized in thin film growth and precipitation reactions.

Interactions:
University of Alberta (D. Mitlin)
Centro Atómico Bariloche (A. Tolley)
ORNL (M. Miller)
RPI (D. Lewis)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Over 20 invited talks since 2004

Personnel Commitments for FY07 to Nearest +/-10%: U. Dahmen PI; V. Radmilovic (staff scientist) 50%, M. Rossell (postdoc) 80%.

Authorized Budget (BA):
FY05 $200K FY06 $192K FY07 $192K

Laboratory Name: Lawrence Berkeley Nat. Laboratory
B&R Code: KC020102

FWP and possible subtask under FWP: Mechanical Properties Program: Hierarchical/hybrid structural materials
FWP Number: KC13
Program Scope:
This multidisciplinary investigation focused on the development of a general understanding of the mechanical behavior of next generation structural materials, in particular involving mechanical properties that are influenced by factors operating at a wide range of length scales. Our long-term goal is to design, synthesize, and characterize (structurally and mechanically) a new series of hierarchical/hybrid structural materials, whose unique properties derive from architectures controlled over multiple dimensions. Using the inspiration of natural materials, the research combines (a) mechanistic understanding of structural behavior at multiple length scales, initially for small number of select polymer/ceramic and metal/ceramic systems, (b) experimental synthesis of such materials, (c) control of structure features at the nanoscale, particularly interfaces, (d) experimental and theoretical characterization at atomic to macroscopic dimensions, and e) evaluation of these (non-biological) materials for technological application.

Major Program Achievements (over duration of support): This program is an outgrowth of the Ceramics Program, which was focused on the characterization and development of structural ceramics, involving studies of the nanoscale intergranular amorphous films (IGFs), and the development of interfacial science and its application to reactive spreading, joining, fracture, and high-temperature oxidation.

In the previous Ceramics Program, a suite of *in situ* toughened ceramics, ABC-SiC, with excellent fracture, creep, wear and fatigue strength to 1350°C was developed with the generally mutually exclusive properties of high low-temperature toughness (due to the glassy IGFs) and excellent high-temperature strength (from *in situ* crystallization of the IGFs). Studies on doped Si_3N_4 provided a direct correlation between the toughness and atomistic computations of IGF structure. Analysis of the R-curve has shown how the small-crack regime is related to the strength of ceramics at realistic flaw sizes. Theoretical cohesive-zone models revealed the mechanisms by which rapid crack-growth resistance can be developed at small crack extensions, and the analysis extended to cyclic fatigue to predict thresholds.

Combined experimental and theoretical studies revealed that due to the stronger interatomic forces, high-temperature spreading is controlled by the atomic dynamics at triples junction rather than by viscous dissipation (as occurs at low temperature). These results will guide the formulation of a unified theory of spreading at high- and low-temperatures.

With our new focus, we are developing an ice-templating technique (freeze casting) to synthesize, for the first time in practical dimensions, new hybrid composites with bio-inspired hierarchical architectures. We have fabricated model "brick-and-mortar" and lamellar alumina-based materials with polymeric or metallic second phases and layer thicknesses varying from ~1 to 200 µm. The technique allows the control of the bridging between ceramic lamellae and of the interfacial roughness and chemistry down to the nanoscale. For example, small Ti additions (0.5 wt.%) increase the strength and toughness of Al_2O_3/Al-Si composites by more than 50% due to Ti segregation at the metal/ceramic interface. Preliminary results indicate that these complex architectures result in materials that exhibit mechanical properties well in excess of those that could be expected from either of the constituent phases.

Program Impact: In addition to defining the influence of the structure and composition of internal interfaces and materials architecture at multiple length scales on the mechanical behavior of materials, a crucial aspect of the work is the formulation of novel processing routes for the fabrication of such complex materials designed from the nano to the meso-level to test and advance these concepts. We believe this to be the path for the development of new families of materials with hierarchical structures yielding unprecedented combination of properties with potential application to all aspects of engineering.

Interactions:
Internal— Advanced Light Source, National Center for Electron Microscopy, NERSC computation facility
External—ORNL; LLNL; SNL; ANL; NIST; MIT; MPI Stuttgart.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
R.O. Ritchie – 2007 A.A. Griffith Medal & Prize (Institute of Materials, UK)

Personnel Commitments for FY07 to Nearest +/- 10%:
R. O. Ritchie (12%), J. W. Ager (10%), D. C. Chrzan (8%), E. Saiz (40%), A. P. Tomsia (30%); 2 Postdocs (50%) 2 Grad. Students (50%)

Authorized Budget (BA):
FY05 $1314K FY06 $1161K FY07 $111610K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP: Electronic Materials Program
FWP Number: MSD KC1201

Program Scope: The Electronic Materials Program advances the fundamental understanding of the materials science of semiconductors. The research focuses on the relationships between synthesis and processing conditions and the structure, properties, and stability of semiconductor materials systems. Progress in these areas is essential for the performance and reliability for technologies that lie at the heart of the DOE mission including ultrahigh efficiency photovoltaic energy conversion devices, high efficiency solid-state sources of visible light, visual displays, and of a large variety of sensors and power control systems for energy generation, conservation, distribution and use.

Major Program Achievements (over duration of support):

- Pioneered scientific applications of isotopically controlled semiconductors; performed definitive impurity and self diffusion studies in Group IV and III-V semiconductors using stable enriched isotope superlattices.
- Developed new theory (band anticrossing model) to explain properties of "highly mismatched" alloys (HMAs) such as GaN_xAs_{1-x} and discovered new II-VI-based HMAs, including the first multiband semiconductor.
- Contributed significantly to the understanding of InN as a narrow gap semiconductor and established p–type doping across the entire InGaN composition range.
- Pioneered the use of pulsed laser melting for the synthesis of highly non-equilibrium alloys, including HMAs and "spintronic" materials.
- Established fundamental relationship between native defects and the achievable limits for doping.
- Identified Mn interstitials as the crucial defects in ferrmomagnetic $Ga_{1-x}Mn_xAs$ and established that these defects lead to a thermodynamic limit on the Curie temperature in this alloy system.
- Developed advanced electron microscopy methods to quantify the growth mechanisms of extended defects and to determine the atomistic core structure of dislocations in group III nitride thin films and heterostructures.
- Developed new theory of nucleation of melting/freezing phase transitions for embedded nanocrystals and verified predictions experimentally.

Program Impact: Under sustained BES funding, the Electronic Materials Program has discovered new classes of semiconducting materials (e.g., II-VI HMAs) and has contributed significantly to the synthesis and fundamental understanding of a large number of elemental and compound semiconductors. Basic research in the Program concerning the interplay of extended defects, compositional fluctuations, and the resulting strain distributions and the light emission mechanism in GaN and InGaN aided the development of solid-state lighting based on this materials system. Most recently, Program research has established that both In-rich InN and certain II-VI and III-V HMAs show promise as entirely new types of high efficiency solar cells and other opto-electronic devices.

Interactions: Internal—National Center for Electron Microscopy, Advanced Light Source. External— Cornell, Purdue, Simon Fraser, Notre Dame, MIT, Münster Univ., Germany, LANL, Georgia Tech, MPI Stuttgart, Inst. High Pressure Physics, "Unipress", NREL, Harvard, Hewlett-Packard, Agilent, Xerox,

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
J. W. Ager III – co-author, "Isotopic Effects in Solids," *Encyclopedia of Condensed Matter Physics*, co-editor, Topical Issue of *Semiconductor Science and Technology*, "Group III-N-V Alloys," 2002.
D. C. Chrzan – Miller Research Professorship, 2004.
O. D. Dubon – Presidential Early Career Award for Scientists and Engineers (PECASE), 2004.
E. E. Haller – Turnbull Award, MRS, 2005; Fellow of AAAS, 2004; James C. McGroddy Prize for New Materials of the American Physical Society, 1999; Chair, 20th Intl. Conf. on Defects in Semiconductors, Berkeley, CA 1999; Max-Planck Research Award, 1994; Research Professor, Miller Foundation for Basic Research in Science, 1990 and 2001; Fellow, American Physical Society, 1986; A. von Humboldt US Senior Scientist Award, 1986.
Z. Liliental-Weber – Chair, IEEE Semiconducting and Insulating Materials Conference, Berkeley, CA 1998.
W. Walukiewicz – Fellow, American Physical Society 2006; R&D 100 Award, 2006; Chair, Gordon Res. Conf. on Defects in Semiconductors 2006; co-editor, Topical Issue of *Semiconductor Science and Technology*, "Group III-N-V Alloys," 2002, NTT distinguished Professorship 1990.
K. M. Yu – R&D 100 Award, 2006.

Personnel Commitments for FY07 to Nearest +/- 10%:
E. E. Haller (20%), J. W. Ager III (40%), D. C. Chrzan (10%), O. D. Dubon, Jr. (10%), Z. Liliental-Weber (60%), W. Walukiewicz (65%), K. M. Yu (60%).

Authorized Budget (BA):

FY05 $1418K	FY06 $1418K	FY07 $1451K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020103

FWP title and possible subtask under FWP: Mechanics at Hard-Soft Materials Interfaces
FWP Number: KC1202

Program Scope: The overall program goal is to advance the fundamental understanding of complex phenomena in soft and hard materials. The research focuses on two areas: (i) understanding of transport of liquids, ions, and biomolecules in ***nanofluidic*** channels: This explores a new class of nanomaterials to study molecular and ionic transport in confined or low-dimensional liquids. (ii) understanding the chemomechanics of reaction-induced mechanical forces, and using it for biological and chemical sensing and actuation.

Major Program Achievements (over duration of support):

- Showed that the ionic conductance in nanochannels is about 10^4-10^5 times higher than predicted by bulk theory.
- Created the first nanofluidic transistor and demonstrated transconductance
- Demonstrated digital control of protein transport in transistor circuits
- Demonstrated an interesting ionic transition during DNA translocation and protein reaction in fluidic nanotubes/nanochannels and showed that it can be used to measure the charge-to-volume ratio of biomolecules
- Experimentally demonstrated nanoscale patterning of molecules inside nanofluidic channels and developed the appropriate reaction-diffusion theory to predict the behavior
- Observed novel phase transition phenomena in nanofluidic channels, which seem to resemble spinodal decomposition
- Demonstrate a ionic diode using nanofluidics channels
- Demonstrated measurement of protease activity using nanochannels
- Developed micro-cantilever and micro-membrane arrays for studying nanomechanics of molecular reactions in high-throughput manner.
- Developed surface chemistry protocols for attachment of biomolecules and preventing biomolecules from nonspecific binding
- Using directed evolution of bacteriophages, created new receptors for small molecules such as DNT and TNT
- Discovered new peptide receptors for methyl-parathion (MTP), a carcinogenic insecticide
- Identified polymeric scaffold for binding peptide receptors for chemically specific coating
- Developed sensor system for portable chemical sensor

Program impact: The impact of studying aqueous solutions of ions and biomolecules could have significant impact on fundamental understanding of water, with implications in water purification, biochemical assays at possibly single cell levels, and electrochemical energy conversion/storage. The development of highly selective receptors for important gas molecules, and then their utilization in chemical sensing addresses a fundamental national need.
Interactions:
Peidong Yang (Dept. of Chemistry, UCB and MSD, LBL); Arup Chakraborty (Depts. of Chem. Engr & Chemistry, UCB and MSD, LBL); Frank Chen (Life Sciences Division, LBL); Ron Zuckermann (Chiron Corp.), Seung-Wuk Lee (Dept. of Bioengineering, UCB and MSD, LBL)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
(i) Elected to National Academy of Engineering; (ii) Member, Nanotechnology Advisory Group, President's Council of Advisors on Sci. & Tech. (PCAST); (iii) Member, Council of Materials Science & Engineering, DOE; (iv) Member, Advisory Committee, Engineering Director of NSF; (v) Heat Transfer Memorial Award; (vi) 20 Academic Invited Talks; 12 Conference Invited Talks; 3 Industry Invited talks.

Personnel Commitments for FY07 to Nearest +/- 10%: (provide name where relevant)
Arun Majumdar (PI): 10 %; 2 Graduate Student: 49.5% 9 month academic year + 100 % 3 month summer (one working on nanofluidics and the other working on peptoids)
Authorized Budget (BA):
FY05 \$230K FY06 \$230K FY07 \$230K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP: Characterization of Functional Nanomachines
FWP Number: MSD KC1203

Program Scope:
Development and application of controllable, operational nanomachines and nanomotors from molecular building blocks. Determination and control of the mechanisms of chemical-to-mechanical energy transfer in naturally occurring molecular biomotors, artificial biomotors, and engineered biochemical assemblies. Chemical synthesis of new molecules having tailored geometry, electro-activity, and surface reactivity for use as nanomachine components. Local probe study of functional molecules adsorbed to surfaces and actuated using optical and electronic stimulous. Use of combined MEMS technology and fullerene growth techniques to create electro-mechanically actuated molecular motors from carbon nanotubes. Theoretical prediction and explanation of nano-motor behavior through *ab initio* electronic structure calculations.

Major Program Achievements (over duration of support):
Observation of reversible photomechanical switching of single-molecules at a surface using azobenzene derivatives. Use of nano-droplet surface tension to create new nanoscale relaxation oscillator. Synthesis and testing of nanotube nanomotor arrays. *ab initio* calculation of electronic structure of *cis* and *trans* states of photomechanically active molecules, new predictions of excited state dynamics of adsorbed azobenzene molecules. Characterization of friction and dissipation of interlayer nanotube bearings. Determination of new mechanisms for mechano-chemical transduction in the packaging motor of bacteriophage phi29, directional translocation on DNA by the protein machine FtsK, and supercoiling action of *E. coli* gyrase. Development of new tip-activated reaction-based lithography technique to create chemically active surface patterns using amine-based chemistry of SAMs on silicon.

Program impact:
First observation of reversible, light-activated single-molecule switch. Fabrication and operation of remotely controlled nanotube-based mechanical motors capable of operation at high and low temperature and in vacuum environment. Control of molecular nanomechanical and self-assembly behavior at surfaces. Theoretical understanding of mechanical energy dissipation mechanisms (friction) in nanotube bearings. Significant progress in characterizing and re-engineering naturally occurring molecular machines and biomotors.

Interactions:
Internal: National Center for Electron Microscopy, National Scientific Computing Center (NERSC), Advanced Light Source, Berkeley Microfabrication Laboratory
External: IBM Almaden, Yale, University of Vienna, Max Planck Institute Stuttgart, University of Pennsylvania, Pennsylvania State University, UCLA, SUNY Stony Brook, Seoul National University, Korea, Hong Kong University of Science & Technology, and Universidad del Pais Vasco, Spain

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
A. Zettl - R & D 100; **M. L. Cohen** - National Medal of Science, APS President; **Carlos Bustamante -** Honorary Degree Doctorate by the University of Chicago**; J Frechet** - 2005 Esselen Award for Chemistry at the Service of Society; **S.G. Louie** - National Academy of Science, Outstanding Overseas Chinese Award; **D. Trauner** - Novartis Young Investigator Award; M. F. Crommie - APS Fellowship

Personnel Commitments for FY07 to Nearest +/- 10%:
1 Principal Investigator (Crommie (25%)))
6 faculty scientists (Bustamante (15%), Cohen (10%), Frechet (15%), Louie (10%), Zettl (20%), Trauner (20%))
5 postdocs (L. J. Berbil-Bautista (100%) R. Case (100%), T. Hugel (10%), P. Zhang (50%), A. Kirakosian (50%))
6 grad. students (M. Comstock (100%), K. Sivula (35%), A. Murphy (100%), G. Begtrup (60%), J. Sau (50%), M. Volgraf (100%))

Authorized Budget (BA):
FY05 $939K FY06 $939K FY07 $940K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP: Nanowire-Based Functional Devices and Assemblies
FWP Number: KC1204

Program Scope: The goal of this research is to develop the science and technology of a broad spectrum of 1-dimensioanl inorganic semiconducting nanostructures or nanowires for energy-related applications. Our approach relies mainly on the vapor-liquid-solid (VLS) process that can be used to grow monocrystalline nanowires Si, Ge, SiGe, GaN, ZnO and various II-VI, III-V semiconductors and their alloys. Significant research efforts have been placed on the fundamental understanding and control of the nanowire nucleation/growth. The fundamental information is then be used to guide the nanowire growth process which would include monodispersity control over size and aspect ratio; growth orientation control, precise site/density control and compositional control. Lastly, both parallel process (Langmuir-Blodgett technique) and serial process (nanomanipulation, optical trapping) are being explored for the hierarchical assembly of these nanowire building blocks for their potential nanophotonic and energy conversion applications. The potential of using these semiconductor nanowires for photonics, solid state lighting, nano-bio interface, photovoltaics and thermoelectrics are being actively investigated.

Major Program Achievements (over duration of support):
(1). One crucial challenge for subwavelength optics has been the development of a tunable source of coherent laser radiation for use in the physical, information, and biological sciences that is stable at room temperature and physiological conditions. Inorganic nanowires have diameters substantially below the wavelength of visible light and have unique electronic and optical properties that make them prime candidates for subwavelength laser and imaging technology. Recently we have reported the development of an electrode-free, continuously-tunable coherent visible light source compatible with physiological environments, from individual potassium niobate ($KNbO_3$) nanowires. These wires exhibit efficient second harmonic generation (SHG), and act as frequency converters, allowing the local synthesis of a wide range of colors via sum and difference frequency generation (SFG, DFG). We use this tunable nanometric light source to implement a novel form of subwavelength microscopy, in which an infrared (IR) laser is used to optically trap and scan a nanowire over a sample, suggesting a wide range of potential applications in physics, chemistry, materials science, and biology.
(2). The InGaN ternary alloy is of interest for solid state lighting and photovoltaics because of the ability to tune the direct band gap of this material from the near ultraviolet (UV) to the near infrared (IR). In an effort to synthesize InGaN nitride, researchers have tried many growth techniques. Nonetheless, there remains considerable difficulty making high quality InGaN films and/or freestanding nanowires with tunability across the entire range of compositions. We have demonstrated for the first time, the growth of single-crystalline $In_xGa_{1-x}N$ nanowires across the entire compositional range from $x = 0$ to 1; the nanowires were synthesized by low-temperature halide chemical vapor deposition (HCVD) and were shown to have tunable emission from the near UV to the near IR. We propose that the exceptional composition tunability is due to the low process-temperature, and the ability of the nanowire morphology to accommodate strain-relaxed growth, which suppresses the tendency toward phase separation that plagues the thin film community.

Program Impact: Develop the fundamental chemistry and physics of 1-dimensioanl inorganic semiconducting nanostructures or nanowires for energy-related applications including nanophotonics and energy conversion.

Interactions: Arun Majumdar; Richard Saykally, Jan Liphdart.

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

2007	Max Planck Lectureship, Max Planck Institute, Stuttgart, Germany
2007	NSF Alan T. Waterman Award.

Personnel Commitments for FY07 to Nearest +/-10%:
P.D. **Yang** (PI) 20%**;** Dan Gargas (Postdoc) 100%; Peter Pauzauskie (Graduate student) 100%. Ruoxue Yan (Graduate student 100%).

Authorized Budget (BA):
FY05 $411K FY06 $411K FY07 $411K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020103

FWP title and possible subtask under FWP: Nanostructured Materials for Thermoelectric Energy Conversion
FWP Number: KC1205

Program Scope: The overall program goal is to investigate the basic science of thermoelectricity in nanostructured materials in order to gain fundamental understanding of how thermopower, S, electrical conductivity, σ, and thermal conductivity, k, can be manipulated independently so that the thermoelectric figure of merit, $ZT = S^2\sigma T/k$, can be maximized. In order to do so, the program focuses on three classes of materials: (i) hybrid organic-inorganic heterostructures; (ii) complex oxides; (iii) bulk semiconductor nanostructures such as arrays and assemblies of nanowires, nanoholes, and nanoparticles in bulk materials.

Major Program Achievements (over duration of support):

- Developed a new statistical method for estimating the electrical conductance of single molecules
- First measurement of the thermopower of single molecule heterojunctions
- Identified the role of chemistry and fluctuations in thermopower of single molecule heterojunctions
- First measurement of the thermal conductance of molecular monolayers
- Demonstrated size dependence of thermopower in PbS and PbSe quantum dot arrays.
- Thermal conductivity reduction by a factor of 5 in nanoparticle embedded complex oxides
- Demonstrated unusually high thermopower in SrLaTiO films
- Demonstrated power factors ($S^2\sigma$) in SrLaTiO films that are comparable to the best BiTe materials
- Identified strong substrate effect in SLTO films deposited on SrTiO substrates and investigated the role of oxygen vacancies.
- New synthesis technique for making Si nanowire arrays at the wafer scale by etching
- Thermal conductivity reduction by a factor of about 100 in etched Si nanowires without reduction of power factor
- Demonstrated ZT of 1 or higher in rough Si nanowires

Program impact: Direct thermal to electrical energy conversion using solid-state thermoelectric devices is attractive because such devices contain no moving parts and are environmentally benign, and produce electricity from waste heat. If it is used world wide to recover waste heat, it could produce about 400 GW of electric power, which is approximately one half the capacity of USA. Furthermore, it could be used for refrigeration and heat pumping as well. Since heating and cooling takes up more than 50 percent of residential and commercial building energy consumption, which is totally about a third of total energy consumption, it is clearly an important issue on the demand side of energy. What prevents the widespread use of thermoelectrics are: (i) performance; (ii) cost effectiveness. Currently, their performance is below 10 percent of the Carnot limit. While five decades of research has led to understanding of the basic attributes of a bulk thermoelectric material, there is no clear roadmap of increasing $ZT = S^2\sigma T/k$ from 1 to 3. If successful, this program could produce new materials that could increase ZT while simultaneously making them cost effective.

Interactions:
Arun Majumdar (Depts of Mechanical Engr & Materials Science and Engr., UCB and MSD, LBL); Peidong Yang (Depts. of Chemistry and Materials Science & Engr., UCB and MSD, LBL); Joel Moore (Department of Physics, UCB and MSD, LBL); Ramesh Ramamoorthy (Departments of Materials Science & Engr and Physics, UCB, and MSD, LBL); Rachel Segalman (Dept. of Chemical Engr., UCB and MSD, LBL)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
(i) Elected to National Academy of Engineering; (ii) Member, Nanotechnology Advisory Group, President's Council of Advisors on Sci. & Tech. (PCAST); (iii) Member, Council of Materials Science & Engineering, DOE; (iv) Member, Advisory Committee, Engineering Director of NSF; (v) Heat Transfer Memorial Award; (vi) 20 Academic Invited Talks; 12 Conference Invited Talks; 3 Industry Invited talks.
Personnel Commitments for FY07 to Nearest +/- 10%: (provide name where relevant) Majumdar (PI) 10%, Moore, Yang, and Ramesh 10% each (co-PIs); 2 postdocs, 2 GSRAs
Authorized Budget (BA):
FY05 $550K FY06 $550K FY07 $550K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP: Spin Functionality through Complex Oxide Heteroepitaxy
FWP Number: KC1206

Program Scope: Development of highly spin polarized thin film materials that will shed light on key unresolved questions in magnetism concerning the nature of magnetism at boundaries of spin-polarized materials and that will facilitate more energy efficient spin-based electronic applications. We are developing novel functional oxide thin films and heterostructures with spin polarized functionality in order to: (i) design and synthesize complex oxide thin film materials with spin polarized functionality; (ii) obtain a fundamental understanding of the nature of magnetism at boundaries; (iii) develop close collaborations with colleagues at Lawrence Berkeley National Lab (LBNL), Argonne National Laboratory (ANL) and other DOE labs; (iv) act as a resource for thin film materials development; (v) train the next generation of scientists in thin film materials synthesis at the undergraduate, graduate and postdoctoral levels.

Major Program Achievements (October 2006 to September 2007):
Oxide junction heterostructures: Developed an understanding of magnetism at oxide interfaces and novel spin dependent transport mechanisms in oxide junction heterostructures based on spinels and perovskites. Junctions with barrier layers of $CoCr_2O_4$, $MnCr_2O_4$ and $NiMn_2O_4$ have all exhibited a high temperature conventional magnetic tunnel junction behavior along with a low temperature spin filter behavior as the barriers undergo a magnetic transition.
Novel oxide interface materials: Developed a novel type of double barrier junction in which we are able to probe the length scale of reconstruction at the interface of two dissimilar insulators. Our studies of junction devices composed of $SrRuO_3/SrTiO_3/LaAlO_3/SrRuO_3$ layers exhibit ohmic behavior unlike the control junctions of $SrRuO_3/LaAlO_3/SrRuO_3$ and $SrRuO_3/SrTiO_3/SrRuO_3$ that exhibit nonlinear transport expected of a tunnel junction. The ohmic behavior of the composite barrier junctions with total barrier thickness as large as 5nm provides, for the first time, a minimum length scale of interface reconstruction at the $SrTiO_3/LaAlO_3$ interface.
Magnetic Oxide Nanostructures: Probed the evolution of magnetic domain structure in polygons of complex magnetic oxide nanostructures via experiment and simulations. Highly spin polarized complex magnetic oxide nanoscale polygons embedded in a paramagnetic matrix have been studied with X-ray photoemission electron microscopy and magnetic force microscopy. Through the variation of the aspect ratios of these polygons, we have been found the magnetic domain state is a competition between shape, strain and crystal structure effects.

Program Impact:
The development of complex oxide thin film materials with spin polarized functionality has provided model systems which shed light on the nature of magnetism at boundaries of spin-polarized materials. Understanding spin polarization at these surfaces and interfaces is a key element in the development of a more energy efficient spin-based electronics.

Interactions:
Lawrence Berkeley National Laboratory, Advanced Light Source: Elke Arenholz, Andreas Scholl, Andrew Doran
Lawrence Berkeley National Laboratory, Molecular Foundry: Bruce Harteneck
Stanford Synchrotron Radiation Laboratory: Michael Toney
Cornell University and Cornell High Energy Synchrotron Source: Joel Brock, Darren Dale
UC Davis: Nigel Browning, Miaofang Chi

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Stanford Synchrotron Radiation Laboratory (SSRL) 2007 Users' Meeting Best Poster Award.

Personnel Commitments for FY07 to Nearest +/-10%:
Y. Suzuki (PI) 20% time for this project (paid 1 month summer salary during August 2007)
M. Liberati (post-doc) 100%
B.B. Nelson-Cheeseman 100% time on this project but paid for 0% time by DOE as she is on fellowship
Franklin Wong 100% time on this project
Virat Mehta 100% time on this project (on departmental fellowship until May 2007)

Authorized Budget (BA):
FY05 $250K FY06 $250K FY07 $250K

Laboratory Name: Lawrence Berkeley Nat. Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP: Nanocomposite Proton Conductors
FWP Number: KC13H

Program Scope:

The program aims to design, synthesize and test rare earth phosphate materials for proton conducting applications in the temperature region of 300-450 degrees Celsius. The program relies on three major approaches: a theoretical understanding of proton conduction in rare earth phosphates employing quantum chemical computation and molecular simulation; the chemical design, synthesis, and proton conductivity measurement of nano-composite materials expected to exhibit facile proton conduction; and the structural and dynamical characterization of the nano-composite materials using a range of advanced characterization methods including nanoscale structural and chemical electron microscopy, vibrational and x-ray spectroscopy, and nuclear magnetic resonance (NMR). Aliovalently-substituted rare earth phosphates and rare earth phosphate glasses are being synthesized and tested for proton conduction. A comparison of theoretical predictions, observed conductivities, and spectroscopic analyses provides an insight into nature of conduction at the atomic level, and directs the synthesis of novel nano-composite rare earth phosphates.

Major Program Achievements (over duration of support):

Lanthanum and Cerium phosphates with modified grain boundaries were synthesized and characterized, showing proton conductivity in amorphous, nanometer grain boundary layers as high as 10^{-3} S/cm at 500^{o}C. First principles computation revealed that proton conduction in rare earth phosphates, such as $LaPO_4$, proceeds by intertetrahedral hopping. Temperature-dependent ^{1}H MAS-NMR results below 150^{o}C confirmed computed proton activation energies for local motion. It was shown that dramatic increases in proton conductivity in La-phosphates resulted from the introduction of Al, Sr, and Ca leading to glasses and glass-ceramics conductors with a conductivity of $\sim10^{-4}$S/cm at 440^{o}C in dry argon, a record to date. The $(LaSrAl)P_xO_y$ glasses have a melting point of about 800^{o}C, and can allow for easy membrane production by common glass processing methods, and may be thermally manipulated further to yield nanocomposite glass-ceramics with even higher expected conductivities. This finding points to way to easily-fabricated thin proton conducting membranes for hydrogen/air fuel cells operating in the technologically advantageous range of 300-500^{o}C.

Structural and functional characteristics determined by TEM, NMR, and Raman and IR spectroscopy of doped La-phosphate glasses have indicated, for the first time, that proton trapping at aliovalent dopants can play a significant role in determining proton conductivities.

Program Impact:

Proton conductors operational in 300-450 ^{o}C have significant potential as hydrogen or biofuels fuel cells membranes, hydrogen separation membranes, sensors, etc. In addition, the possibility of membrane-forming methods similar to those employed in the glass industry offer considerable practical and economic advantage.

Personnel Commitments for FY07 Nearest +/- 10%:

De Jonghe(20%), Reimer(10%), Ross(10%), 4 postdocs(100%), 4 students (100%)

Authorized Budget (BA):

FY05 $850K FY06 $850K FY07 $850K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020202

FWP and/or subtask Title under FWP: Superconductivity
FWP Number: KC2201

Program Scope: Low- and high-T_c Superconducting QUantum Interference Devices (SQUIDs) and their application to a broad range of phenomena. NMR and MRI in ultralow magnetic fields; zero-field magnetic resonance imaging; novel microstrip resonator configuration for quantum-limited detection; studies of nanomagnets; theoretical limitations of SQUIDs. Specific-heat measurements to investigate relations between structure and physical properties of materials, including superconductors.

Major Program Achievements: Exactness of Josephson voltage-frequency relation. Discovery of quasiparticle charge imbalance in superconductors. Low-noise dc SQUIDs and noise theory in thermal and quantum limits. Measurement of zero-point noise in Josephson junctions. Remote reference technique for magnetotellurics. Observation of nuclear spin noise. Quantitative measurement of macroscopic quantum tunneling and quantized energy levels in Josephson junctions. Demonstrated that l/f noise in SQUIDs arises from both critical current and flux fluctuations. High-T_c SQUIDs using multilayer technology. Development of scanning SQUID microscope. Development of near-quantum limited microstrip SQUID amplifier. Development of SQUID multiplexer. NMR and MRI in microtesla fields. Temperature scales and techniques for specific-heat measurements; applications to ^{4}He, ^{3}He, magnetic materials, nanotubes, and superconductors (e.g., heavy-fermion, high-T_c cuprates, MgB_2, $Na_{0.3}CoO_2 \cdot 1.3\ H_2O$).

Program Impact: (JC): Theory of signal and noise in dc SQUIDs universally used for designing and evaluating practical devices. Observation of quasiparticle charge imbalance led to new experiments and theories. Remote reference technique for magnetotellurics widely adopted. Observation of energy level quantization in Josephson junctions ultimately resulted in a new kind of quantum bit. Technique for reducing l/f critical current noise in SQUIDs widely used for both low-T_c and high-T_c SQUIDs. Ultralow magnetic field technique for NMR and MRI has been adopted in both the U.S. and Europe. (NEP): Measurements on superconductors have contributed to an understanding of the phenomenon.

Interactions: Internal: (JC): E.L. Hahn (Physics, UCB); B. Inglis, (Brain Imaging Center, UCB); D-H. Lee (Physics, UCB); J.W. Morris (MSD, LBNL and Materials Sciences, UCB); A. Pines (Chemistry, UCB and MSD, LBNL); P.L. Richards (Physics, UCB); I. Siddiqi (Physics, UCB); H. Spieler (Physics, LBNL). (NEP): D-H. Lee (Physics, UCB); A. Zettl (Physics, UCB and MSD, LBNL).

External: (JC): D. DiVincenzo (IBM); D. Kinion (LLNL); R. Kleiner (Tuebingen); R.H. Koch, (IBM); D. Koelle (Tuebingen); J. Kurhanewicz (UCSF); D. Larbalestier (Wisconsin); M. Mück (University of Gießen, Germany); M. Shuman (UCSF); J. Simko (UCSF); A. Trabesinger (Zurich); A.V. Ustinov (Erlangen). (NEP): J. Flouquet (CEA, Grenoble); C. Meingast (Forschungszentrum Karlsruhe).

Recognitions, Honors and Awards: (JC): Fellow, AAAS, APS, Royal Society, IOP; Executive Committee, DCMP, APS, 1998-2002; California Scientist of the Year, 1987; London Award, 1987; Division of Materials Sciences Award for Significant Implications for DOE-Related Technologies, 1992; Keithley Award, APS, 1998; Comstock Prize, NAS, 1999; IEEE Award for Significant and Continuing Contributions to Applied Superconductivity, 2002; Scientific American 50 Award, 2002; Lounasmaa Prize, Finnish Academy of Arts and Sciences, 2004; Hughes Medal, Royal Society, 2004; (NEP): Fellow, AAAS, APS; NSF Senior Fellow; Guggenheim Fellow; Professor Invité, Université Joseph Fourier; Alexander von Humboldt Research Award; Invited Lecturer in Physics, NSC, Republic of China; Huffman Award.

Personnel Commitments for FY07 to Nearest +/- 10%:
J. Clarke 15%; N.E. Phillips 5% (charged to project) (program leaders); research chemist (25%): R.A. Fisher (charged to project 5%); gsr's (62.5%): N. Kelso, M. Hatridge, S. Busch, Daniel Slichter (zero-time charged to project); postdocs (100%): D. Kinion (zero time charged to project), F. Hardy (17%), S. Michotte (zero time charged to project), M. Moessle (30% charged to project); admin. (75%): B. Salisbury.

Authorized Budget (BA):

FY05 $485K	FY06 $485K	FY07 $485K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC20202

FWP and possible subtask under FWP: Quantum Materials Program
FWP Number: KC2202
Program Scope: "Quantum materials," systems in which the quantum-mechanical correlations of electrons play a dominant role, manifest a rich and diverse spectrum of physical phenomena. In such materials interacting charge, spin, orbital, and lattice degrees of freedom create a multi-dimensional phase space that make possible novel phases of matter and new functionalities. We are carrying out a research program in which fundamental understanding of the novel phases and elementary excitations of bulk crystalline transition metal oxides serves to inform and guide our development of new functionality in oxide heterointerfaces and other artificially prepared nanostructures. The core QM team consists of Birgeneau, Bourret-Courchesne, Lanzara, Lee, Orenstein, Ramesh and Vishwanath. We collaborate with other members of the MSD and LBL community (Hellman, Dahmen, Suzuki, Scholl, Rotenberg, Kortwright, Moore,) to leverage the investment.
Major Program Achievements (over the duration of the program): A major effort in the past year has been the establishment of a modern oxide single crystal growth facility led by **Birgeneau/Bourret-Courchesne**. This will position us to create a broad spectrum of correlated oxides in large single crystal form for detailed measurements. The Bourret-Courchesne's group has focused on setting up the crystal growth facility. In the past year the Birgeneau group has completed and published a study of the high energy spin excitations in the material YBa2Cu3O6.35 (Tc=18K) which is weakly superconducting. They find that the excitations look like conventional spin waves up to energies of order the pseudo-gap and then they both broaden and soften at higher energies. The main scientific focus of the **Lanzara's** group this year has been to understand the role of electron lattice interaction and competing orders as charge density wave (CDW) in correlated materials as well as to understand the electronic structure and the unique properties deriving from it, of Dirac fermions in graphite/graphene. In the field of carbon based materials, we have been the first group to perform angle resolved photoemission experiments on graphene and provide the first experimental evidence on the existence of Dirac quasiparticles in graphite. We have shown that although the carrier density is close to zero, disorder can affect locally the density of graphite leading to the coexistence of electron and hole regions. Some of these works are the result of the active collaboration between the **Lanzara's** and the **Lee's** group. The general theme of **Lee's** research this year is the study of 1) electron-lattice interaction, 2) competing order, and 3) possible interfacial electronic states in strong correlated materials. In addition, **Lee** is working on understanding the electronic structure of graphene (Lanzara) and the nature of ferroelectric order in BFO (Orenstein and Ramesh). In collaboration with the Ramesh group, **Orenstein** is using optical second harmonic generation (SHG) to probe the symmetry and dynamics of the polarization, **P**, in the model multiferroic compound $BiFeO_3$. Research in the **Ramesh** group is focused on creating epitaxial heterostructures and nanostructures using highly correlated, multifunctional oxides as building blocks. A strong collaboration with Orenstein and Lee is focused on understanding the fundamental properties of the multiferroic perovskite BiFeO3. Using epitaxial growth by laser MBE, conventional MBE and CVD, we have been able to create model thin film heterostructures in various orientations with controlled domain structures. They are being probed using a combination of SHG (Orenstein), XMLD-PEEM(Scholl/Arenholz), and PFM (Ramesh). We have demonstrated that there is indeed coupling between ferroelectricity and antiferromagnetism. Using this, we have built ferromagnet-multiferroic heterostructures to explore pathways to control ferromagnetism with an electric field. The **Vishwanath** group worked mainly on frustrated magnetism during this period, and also on the effect of novel magnetic orders on transport properties in metallic magnets. In frustrated magnets, the dominant interactions do not determine a unique ground state. A large degeneracy prevails at the classical level. Therefore weak interactions, such as coupling to the lattice, can play a decisive role in determining the ground state and lead to complex orders. These complex magnetic orders often lead to multiferroic behavior, where ferroelectric polarization is induced by the magnetism.
Recognition, Honors, and Awards (at least partly attributable to support under this FWP or subtask):
Lanzara : ALS Shirley Award**;** *Ramesh:* MRS TurnbullLectureship-MRS; *Orenstein:* APS Isakson Prize; *Vishwanath:* NSF Career Award.
Relationship to other projects. The Quantum Materials program is highly leveraged in terms of interdisciplinary collaborations within LBL as well as outside (i.e., other national labs and academic institutions). A significant component of our research is carried out in collaborations with scientists at the ALS, NCEM and Molecular Foundry. Suzuki, Lanzara and Ramesh are key users of various beamlines at the ALS for magnetic studies of complex oxide heterostructures and nanostructures as well as spectroscopy and collaborate extensively with Scholl, Arenholz, Rotenberg, and Kortright. Strong collaborations with scientists at the NCEM (Dahmen, Browning, Kieselowski, Schmid), in the area of energy loss spectroscopy and high resolution imaging of interfaces are already in place. We also have external collaborations with other National Labs (Argonne, BNL, ORNL) and academic institutions.
Personnel Commitments FY07 +/10%: Orenstein 35%, Ramesh 10%, Vishwanath 20%, Lanzara 20%, Lee 15%., Bourret-Courchesne 15%. Postdocs and students hired in FY07 = 9 FTE.
Authorized Budget (BA):

FY05 $962K	FY06 $1012K	FY07 $1268K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP: Ultrafast Materials Science
FWP Number: KC2203

Program Scope: Advanced ultrafast techniques applied to fundamental problems in condensed matter physics, including: (i) complex and highly-correlated materials exhibiting new physics, and (ii) exotic properties; and novel physics at surfaces, interfaces, and in nanostructured materials. Ultrafast THz, visible, and x-ray spectroscopy provides new insight to charge, spin, quasiparticle, and structure dynamics by separating correlated phenomena in the time domain. Ultrafast technology underpins unique nonlinear spectroscopies for probing surfaces and interface properties of liquids, polymers, and related solids.

Major Program Achievements: *Carrier dynamics in semiconductors*: scattering and dephasing dynamics demonstrated to be strongly dependent on system dimensionality, coherence of indirect excitons ideally-suited for creating a degenerate Bose-gas; elucidated dynamics of 2D electron gas (2DEG) in large magnetic field and influence of 2DEG on the coherence of *e-h* pairs in the quantum Hall regime; first observation of degenerate and spatially-ordered exciton states; first demonstration of THz stimulated emission from intra-exciton transitions; first measurement of spin diffusion coefficient of 2DEG and direct evidence of spin-Coulomb drag. *High-T_c Superconductors (HTS) and transition-metal oxides (TMO)*: pioneered research in THz optical conductivity of HTS including observation of optical Hall conductivity of quasiparticles and vortices; measurement of quasiparticle scattering in BSCCO revealing bimolecular kinetics of Cooper-pair formation; direct measurement of phase fluctuation rates of the superconducting (SC) order parameter and demonstration that they drive the SC/normal phase transition; first direct measurement of quasiparticle propagation (diffusivity tensor, and scattering rates) in a HTS; revealed the dominant band-like (v.s. Mott-Hubbard) character of the insulating state of VO_2; first evidence of an ultrafast insulator-metal transition (IMT) via vibrational pumping in PCMO. *Ultrafast x-ray science*: first demonstration of femtosecond pulses from a synchrotron; first time resolved x-ray spectroscopy of the ultrafast IMT in VO_2; first quantification of atomic displacements of coherent polariton mode in $LiTaO_3$; dynamic ligand dilation observed in ultrafast spin transition in TMO molecular complex. *Surface/Interface Physics*: new understanding of surface/interface properties of water, ice, and numerous other liquids and solids; pioneered the development of sum-frequency spectroscopy to study surface reactions under ambient conditions, and as a sensitive probe of molecular chirality with applications to *in-situ* study of biomolecules; developed powerful optical technique to study surface chemical diffusion of atoms and molecules with sensitivity to anisotropy, concentration, impurities, etc.

Program Impact: This program has generated new fundamental knowledge of electronic and atomic dynamics in condensed matter. Results from semiconductors, correlated electron systems, nanostructures, surfaces, and molecular complexes have challenged previously held assumptions and advanced new paradigms to describe the dynamic behavior that underpins novel material properties and functionality.

Interactions: Internal: LBNL Materials Science Div., Chemical Science Div., Earth Science Div., Advanced Light Source. External: U.C. Berkeley Physics Dept., Chemistry Dept., Stanford Univ., U.C. Santa Barbara, U.C. San Diego, U. Illinois, Michigan State, Naval Res. Lab., U. British Columbia, U. Tokyo, Tokyo Inst. Tech., CRIEPI Japan, Ecole Normale Superieure de Paris, Acad. Sinica Taiwan, Wietzmann Inst.

Recognitions, Honors and Awards (in part attributable to program support): *D. Chemla*: Member Nat'l Acad. Sci. (1997), Quantum Elect. Award (IEEE, 1995), Humboldt Prize (1995), Gordon Conf. Cruikshank Lecturer (1995); *J. Orenstein*: Isakson Prize (APS, 2008), Chair Gordon Conf. on Correlated Elect. Sys. (2002-06); *R. Schoenlein*: Lomb Medal (OSA, 1992); *Y.R. Shen*: Townes Award (OSA, 1986); Schawlow Prize (APS, 1992); Dist. Traveling Lecturer (APS, 1994-96); Max Planck Inst. Res. Award (1996); Chancellor's Prof. Berkeley (1997-2000); DOE Materials Sci. Award (1997); D.Sc. Honoris Causa, Hong Kong Univ. of Sci. and Tech. (1997) and Nat'l. Chao Tung Univ., (1998); Isakson Prize (APS, 1998); Member Nat'l Acad. Sci. (1995); Amer. Acad. of Arts & Sci.(1990), Acad. Sinica (1990), Foreign Member, Chinese Acad. of Sci. (1996); Hon. Chair Prof. Nat'l. Tsing Hua Univ. (2001-07).

Personnel Commitments for FY07 to Nearest +/- 10%:.D. Chemla (P.I.) 10%, R. Kaindl (Staff. Sci) 100%, J. Wang (Postdoc) 100%, I. Cotoros (GSRA) 35%, K. Dani (GSRA) 100%; J. Orenstein (P.I.) 30%, M. Langer (GSRA) 100%, C. Kantner (GSRA) 50 %; R. Schoenlein (P.I.) 70%, M. Rini Postdoc (100%); Y.R. Shen, (PI) 50%, J.McGuire (GSRA) 50%; Ji Na (GSRA) 50%, L. Zhang (GSRA) 50%.

Authorized Budget (BA):
FY05 $1244K FY06 $1223K FY07 $1207K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP: Synthesis and advanced characterization of nanoscale magnetic materials
D.T. Attwood, C.S. Fadley, P. J. Fischer, F. Hellman, J.B. Kortright
FWP Number: KC2204

Program Scope: Novel magnetic nanoscale structures are synthesized and characterized with advanced techniques. The systems studied include vapor-phase deposited thin films and multilayers, structured or self-assembled nanoscale systems, nanoparticles, amorphous materials, metastable alloys, complex oxides, ferroelectric and multiferroic films, and nanocrystalline and single-crystal materials relevant to applications in spintronics and magnetics. Properties of interest include exchange bias; giant-, tunnel- and colossal- magnetoresistance; half-metallic ferromagnetism; and current-induced phenomena. Nano-calorimetric measurements yield electron, phonon, and magnon densities of states, as well as magnetic ordering temperatures. Advanced synchrotron-radiation techniques yield element-specific electronic and magnetic structures, including spatial resolution from micron to sub-nanometer scale, as well as time resolution to the picosecond scale. The methods include resonant soft x-ray scattering, soft x-ray microscopy, and high resolution spectroscopies (core- and valence- photoelectron, x-ray absorption, x-ray emission and inelastic scattering) excited by standing waves.

Major Program Achievements (This recently established group combines four established thrust areas)**:**

Synthesis and Calorimetry (Hellman):
- Significant improvements in micro/nanocalorimetry devices.
- Determination of thermodynamic properties of thin-film amorphous Si and Si-N.
- Development of a cluster model for perpendicular anisotropy in CoPt3 films.

Resonant soft x-ray scattering (Kortright):
- New insight into exchange-bias mechanism from depth-resolved magnetic reflectivity.
- Resolution of dipolar and exchange interaction effects in heterogeneous films and nanoparticle assemblies.
- Demonstration of molecular bond specific scattering at carbon *K* edge in heterogeneous polymer films.

Soft x-ray microscopy (Attwood, Fischer):
- Magnetic x-ray imaging of spin current induced domain wall motion in ferromagnetic domain wires with high spatial and temporal resolution.
- Pioneering studies of the nanoscale stochastic character in magnetization reversal and spin torque phenomena.
- Development of phase contrast imaging using novel Fourier optical techniques.

Soft x-ray spectroscopy (Fadley):
- Standing wave excited depth-resolved studies of electron and x-ray signals in GMR and MTJ systems.
- Observation of high-T electron localization in LSMO using multiple soft x-ray spectroscopies.
- Study of the oxidation at Si surfaces at multitorr pressures with time-resolved photoemission.

Program impact:
Development of new nanocalorimetric, soft x-ray scattering, soft x-ray microscopic and X-ray optics, and standing-wave spectroscopic techniques, and application of them to novel magnetic materials and nanostructures

Interactions:
A. Navrotsky (UCD)-calorimetry; D. Smith (ASU)-high-res. TEM, J. Mitchell (ANL)-oxide samples; R. Ramesh and Y. Suzuki (UCB), S.S.P. Parkin (IBM Almaden), E. Fullerton and I. Schuller (UCSD), K. Liu (UCD)-magnetic nanostructures; A. Epstein (OSU)-molecular magnets; H. Ade (NC State)-polymers; G. Meier (U Hamburg)-spin torque/transport; D. Allwood (Sheffield)-spintronic logic; G. Panacionne and F. Parmigiani (Trieste), C. Schneider (Jűlich), W. Wurth (U. Hamburg)-synchrotron radiation spectroscopy

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Hellman--APS Keithley Instrumentation Award; Fadley--Helmholtz-Humboldt Research Award ('06)

Personnel Commitments for FY07 to Nearest +/- 10%: C.S. Fadley (50%)

Authorized Budget (BA:
FY05 $2428K FY06 $2250K FY07 $2405K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP: A Synergistic Approach to New Hydrogen Storage Materials, Part II
FWP Number: KC2205
Program Scope: This research is intended to generate new types of hydrogen storage materials with the potential for meeting the criteria required for making hydrogen fuel cell-powered vehicles feasible. In particular, nanostructured materials, such as boron nitride nanotubes and metal nanocrystal arrays, with the potential for attaining a reversible uptake of 6 wt % H_2 while operating at moderate temperatures and pressures are sought. A coordinated theory effort is in place to guide the experiments.

Major Program Achievements (over duration of support):
(1) A Sieverts apparatus for the volumetric measurement of H_2 adsorption isotherms has been purchased, installed, and tested.
(2) Both CVD and induction furnace methods have been refined for the large scale synthesis of pure BN nanotubes.
(3) Conditions for varying the morphology of nanostructured BN have been identified.
(4) CVD methods have been developed for the generation of composites of BN nanoparticles and metal or metal oxide nanoparticles.
(5) Plasma-based methods have been developed for the implantation of C atoms in BN nanotubes.
(6) Plasma-based methods for functionalizing BN nanotubes with amine groups have been developed. This has further enabled coating of the nanotubes with a variety of different metal nanocrystals.
(7) Computational efforts have demonstrated a higher H_2 binding affinity for BN nanotubes compared to carbon nanotubes. In addition, the role of defect structures in enhancing H_2 binding has been explored.
(8) Computational work has been carried out probing the effects of B- and N-doping in graphene sheets for stabilizing surface-bound metal atoms. The changes in H_2 binding characteristics upon variation of the metal atom have also been calculated.
(9) A method has been developed for generating three-dimensional arrays of Pd nanocrystals with variation in diameter. Means of characterizing the hydrogen storage properties of such nanocrystal arrays have been devised.

Program Impact: The synthesis and characterization methods developed in the course of this program will be of value to other investigators in the field. Moreover, the new materials produced may ultimately serve as components of hydrogen storage systems for hydrogen fuel-cell powered vehicles.

Interactions: Close ties are maintained with the principle investigators and coworkers involved in Part I of this program (Jean Fréchet, Martin Head-Gordon, Jeffrey Long, and Thomas Richardson) and with Sandia National Laboratory, Hydrogen Storage Program (Lennie Klebanoff, director)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Alivisatos: ~30 plenary and invited lectures last year, including seven endowed lectureships; NSF Presidential Young Investigator, Sloan Foundation Fellow, Exxon, ACS Solid State Chemistry Fellowship, MRS Outstanding Young Investigator, Wilson Prize, Harvard, Fellow APS, Fellow AAAS, Visiting Professor St. John's College Cambridge, Colloid and Surface Chemistry ACS Award, elected to the National Academy of Sciences and the American Academy of Arts and Sciences, Larry and Diane Bock Chair in Nanotechnology, University of Chicago Distinguished Alumni Award, Rank Prize for Optoelectronics Award. *M. L. Cohen* – Fellow of APS; member of National Academy of Sciences; Sloan Fellow; Guggenheim Fellow; APS Buckley Prize; DOE Outstanding Accomplishment in Solid State Physics Award; DOE Sustained Outstanding Accomplishment in Solid State Physics Award; APS Lilienfeld Prize; U.S. National Medal of Science; ISI's top 100 most-cited physicists; President of the American Physical Society; member of American Philosophical Society; Foresight Institute Richard P. Feynman Prize in Nanotechnology; Harvard University Loeb Lecturer; University of Montreal Doctorat Honoris Causa; 50 invited talks since 2004. *S. G. Louie* – Fellow of APS; member of National Academy of Sciences; Sloan Fellow; Guggenheim Fellow; DOE Sustained Outstanding Research in Solid State Physics Award; APS Aneesur Rahman Prize; APS Davisson-Germer Prize; ISI's top 100 most-cited physicists; Foresight Institute Richard P. Feynman Prize in Nanotechnology; Outstanding Overseas Chinese Award; University of Chicago Closs Lecturer; Fellow of American Association for the Advancement of Science; 55 invited talks since 2004. *Zettl*: LBNL Outstanding Performance Award 2004, R&D 100 Award 2004, over 33 invited talks since 2003

Personnel Commitments for FY07 to Nearest +/-10%: Long (PI) 10%, Rachel Smith (post-doc) 100%, Toby Sainsbury (post-doc) 100%
Authorized Budget (BA):

FY05 $0535K	FY06 $535K	FY07 $535K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP: Experimental and Theoretical Investigations of Spin Transport
FWP Number: KC2206
Program Scope:
Conventional microelectronic devices are based on the ability to store and control the flow of electronic charge. However, the increasing amounts of power required by modern CMOS-based logic and memory devices is now a critical problem. Spin-based electronics promises a radical alternative, offering the possibility of logic operations with lower power consumption than equivalent charge-based logic operations. Our research team has the necessary experimental and theoretical skills to conduct research into the fundamental physics in support of a spin-based technology. Through collaboration with Prof. David Awschalom at UCSB, we have the ability to design and fabricate quantum well structures with tuned spin-orbit interactions. At LBNL, we have developed the transient spin grating technique for direct measurement of spin current. Finally, these capabilities are linked with a strong theoretical team at Stanford, led by Prof. Zhang.

Major Program Achievements (over duration of support):
Spin-Couomb drag: We have definitively observed a frictional force that opposes spin current in semiconductors. This force, known as "spin-Coulomb drag," had been theoretically predicted but not previously observed because of inability to quantitatively probe spin-diffusion coefficients. The existence of this frictional force, which acts specifically on spin current and not charge current, must be considered in the design of any spin current based device. **Persistent spin helix (theory):** We have investigated the spin dynamics that arise in a two-dimensional electron gas in the presence of both Rashba and Dresselhaus terms in the spin-orbit Hamiltonian. We have shown that an exact SU(2) symmetry arises when these terms are equal, leading to extremely long spin coherence times for certain spin helical states. **Persistent spin helix (experiment):** We have directly observed, using the spin transient grating technique, the enhanced lifetime of a spin helix state that arises when Rashba and Dresselhaus interactions coexist in the two-dimensional electron gas. By adusting the asymmetry of the doping, we have designed samples for which the Rashba spin-orbit strength is approximately the same as the Dresselhaus coupling. This has led to the observation of spin-helix lifetimes of approximately 1ns, during which time each electron diffuses over multiple wavelengths of the grating.

Program impact:
Spin-based electronics promises a radical alternative to charge-based logic operations, offering the possibility of logic operations with much lower power consumption. To exploit the energy-saving potential of spin currents it is essential to be able to control them, as we control the flow of charge. Historically, spins have been manipulated by magnetic fields, which are difficult to control on the nanoscale. Recently it has been recognized theoretically that through spin-orbit coupling it is possible to manipulate spin currents *via* electric fields . In contrast to magnetic fields, nanoscale control of electric fields forms the basis of current integrated circuit technology and is therefore very highly developed. Electric-field control of spin, *via* spin-orbit coupling, will provide a far easier path to adopt spin-based devices into the mainstream of technology.

Interactions: Stanford University (Prof. S. Zhang); UC Santa Barbara (Prof. David Awschalom)

Recognitions, Honors and Awards: American Physical Society Isakson Prize (2008)
Chair, Gordon Conference on Correlated Electron System (2002-2004)
International and national invited talks, including APS March Meeting, Aspen Center for Physics, Institute for Theoretical Physics (Santa Barbara), International Center of Physics (Trieste), Gordon Conference on Superconductivity (Oxford, UK), and Symposium on SPC Coupled Materials (Tokyo).

Personnel Commitments for FY07 to Nearest +/- 10%: J. **Orenstein** (group leader) 30%, Jacob Koralek (postdoc) 100 %

Authorized Budget (BA):

FY05 $0K	FY06 $122K	FY07 $122K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP: Novel sp^2-bonded Materials

FWP Number: KC2207

Program Scope:
Ab-initio quantum mechanical calculations to predict new materials structures and relate them to electronic structure and mechanical and thermal properties. Experimental synthesis of novel sp2-bonded materials including functionalized nanostructures, and characterization using SEM, TEM, STM, AFM, XRD, mechanical properties, and transport properties. Nanoscale device fabrication and testing. Strong connection between theory and experiment.

Major Program Achievements:
Friction and dissipation investigated experimentally for sp^2-bonded nanostructures, including nested nanotubes. Limits placed on dissipation. Theoretical analysis of nanoscale dissipation. Prediction of new nanostructures including nanotubes and nanoparticles containing carbon, boron, and nitrogen. Theoretical analysis of nanparticles and hybrid structures and devices, including optical properties. Functionalization of carbon and boron nitride nanotubes, including biocompatibility enhancement of carbon nanotubes. Demonstration of living cell nanoinjector. Exploratory electronic and mechanical studies of graphene and graphene related materials, both experimental and theoretical.

Program impact:
Lowest friction record for real materials. Experimental demonstration of nanotube cell injection devices, with implicatons for cell function and manipulation. Exciton behavior examined in detail in semiconducting and metallic nanosystems, leading to demonstration (theoretical and experimental) of exitons in 1-D metal. Discovery of new classes of funtionalized BN nanotubes, with relevance to catalysts, photo-devices, and biosystems scaffolding.

Interactions:
Internal: Molecular Foundry, National Center for Electron Microscopy, National Scientific Computing Center (NERSC), Advanced Light Source, Berkeley Microfabrication Laboratory
External: CNRS France, University of Vienna, Max Planck Institute Stuttgart, University of Pennsylvania, Pennsylvania State University, UCLA, SUNY Stony Brook, Seoul National University, Korea, Hong Kong University of Science & Technology, and Universidad del Pais Vasco, Spain

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Alex Zettl – James McGroddy New Materials Prize, Miller Professorship
C. Bertozzi - Molecular Foundry Directorship.
M. L. Cohen -ISI's top 100 most-cited physicists
S. G. Louie –ISI's top 100 most-cited physicists
M. Crommie – Numerous invited talks

Personnel Commitments for FY07 to Nearest +/- 10%:
PI's (Zettl 25%, Bertozzi 10%, Cohen 25%, Louie 20%); Visiting Scientist: (Capaz, - fellowship 50%); Post Docs (Son 75%, Kirakosian 100%, Wiachwiak 100%, Kis 100%, Ikuno 50%, Sainsbury 20%,); GSR's (Khoo 50%, Luo 50%, Fennimore 50%, Mickelson 50%, Begtrup 25%, Yuzvinsky 25%, Chang 25%, Jensen 25%, Girit 25%, Kessler 25%, Huang 25%, Comstock 50%, Chen 50%)

Authorized Budget (BA):
FY05 $1254K   FY06 $1050K   FY07 $1000K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020203

FWP and possible subtask under FWP: Quantum Theory of Materials
FWP Number: KC2301

Program Scope: The emphasis of our research is on carrying out quantum-mechanical calculations for realistic systems based on microscopic first-principles approaches. Model systems are also examined, and new theoretical techniques are developed. Studies include bulk materials, fullerenes, nanotubes, nanowires, graphene and graphene nanoribbons, superconductors, surfaces, materials under high pressure, polymers, clusters, and defects in solids. Close collaboration with experimentalists is maintained. In addition, our program has a new component on strongly correlated systems. This involves developing phenomenological models for phenomena in complex oxides, exact solution of strong correlated models, and exploring physics beyond the Landau paradigm. Strong interaction with experiments are maintained.

Major Program Achievements (over duration of support): Explained properties of materials (e.g., bonding and structural properties; band structure and optical properties; properties of defects, surfaces, clusters and nanostructures) and predicted new materials and phenomena (e.g., superhard materials, new class of nanotubes, new phases of materials under high pressures, new superconductors, excitons in semiconducting and metallic nanotubes). Developed new theoretical and computational methods. In strongly correlated physics, a generalization of the Jackiw-Rebbi theory for fractional charged solitons in 1D to 2D has led to construction of well-controlled theoretical models possessing spin-charge separated excitations, a major challenge for the last twenty years.

Program Impact: Led to discoveries of new materials and properties, explanation of experiments, and development of theoretical methods. Understand of mechanism for fractionally charged excitations in two dimensions and above, pushing the envelope of condensed matter theory beyond the Landau paradigm.

Interactions: Internal—NERSC/LBNL (Canning, Wang), MSD/LBNL (Crommie, Frechet, Lanzara, Trauner, Zettl), CSD/LBNL (Fleming, Head-Gordon); Molecular Foundry/LBNL; Advance Light Source, LBNL; UC Berkeley COINS; External—Yale, Harvard, Cornell, Stanford, U of Washington, Palo Alto Research Center, LLNL, Georgia Tech, Penn State, SUNY Buffalo, U of Texas at Austin; International—Tokyo Inst.of Techn. (Japan), Seoul National U. (South Korea), Korea Advanced Inst. of Science (South Korea), IU. Pais Vasco (UPV/EHU, Spain), KITP (Beijing, China), Fudan Univeristy (China); Center for Advanced Study (Tsinghua University, China).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
M. L. Cohen – Fellow of APS; member of National Academy of Sciences; Sloan Fellow; Guggenheim Fellow; APS Buckley Prize; DOE Outstanding Accomplishment in Solid State Physics Award; DOE Sustained Outstanding Accomplishment in Solid State Physics Award; APS Lilienfeld Prize; U.S. National Medal of Science; ISI's top 100 most-cited physicists; President of the American Physical Society; member of American Philosophical Society; Foresight Institute Richard P. Feynman Prize in Nanotechnology; Harvard University Loeb Lecturer; U of Montreal Doctorat Honoris Causa; Technology Pioneer Award of the World Economic Forum; F.A. Matsen Regents Endowed Lecturer, U of Texas at Austin; W. H. Zachariasen Memorial Lecture, U of Chicago; 55 invited talks since 2005. **D.-H. Lee** – Fellow of APS; Cheung-Kong Chair Professor, Center for Advanced Study, Tsinghua University, Beijing, China. **S. G. Louie** – Fellow of APS; member of National Academy of Sciences; Sloan Fellow; Guggenheim Fellow; DOE Sustained Outstanding Research in Solid State Physics Award; APS Aneesur Rahman Prize; APS Davisson-Germer Prize; ISI's top 100 most-cited physicists; Foresight Institute Richard P. Feynman Prize in Nanotechnology; Outstanding Overseas Chinese Award; University of Chicago Closs Lecturer; Fellow of American Association for the Advancement of Science; Distinguished Research Chair Professor, National Taiwan University; 64 invited talks since 2005.

Personnel Commitments for FY07 to Nearest +/- 10%:
Principal Investigators (Cohen 20%, Lee 80%; Louie 20%); Postdoctorals (F. Giustino 100%; H. Zhai 100%); Grad students (J. Noffsinger 50%; D. Strubbe 50%).

Authorized Budget (BA):

FY05 $315K	FY06 $334K	FY07 $334K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020203

FWP and/or subtask Title under FWP:
Predicting the Electronic Properties of 3D, Million-Atom Semiconductor Nanostructure Architectures
FWP Number: KC2302

Program Scope: To develop new computational approaches for thousand atom nanostructure calculations. Especially to develop the charge patching method, so the electronic structures and optical properties of thousand atom nanocrystals can be calculated with ab initio accuracy, replacing the empirical pseudopotential method, also to calculate the electronic structures of multicomponent nanostructure architectures.

Major Program Achievements (over duration of 2006-2007):
Nanostructure polarization model based on charge patching method (CPM): we have developed a polarization model to describe the charge response of a nanostructure under long range electric field. The motif responses from different atoms are added together to provide the overall response of a nanostructure. This approach can be used to carry out charge density selfconsistent calculations within CPM.

Core/shell nanowires for solar cell applications: using ZnO/ZnS and GaN/GaP as core/shell nanowires, we have calculated the overall reduction of the band gap due to the type II band alignments. This reduction significantly increases the theoretical solar cell efficient. Because the electron will be located at the ZnO or GaN core, while the hole will localize in the ZnS or GaP shell, this will help the electron/hole charge separation. Our paper [Nanolett. 7, 2377(2007)] is the number 10th most accessed article published in Nanolett. in the third quarter of 2007.

Acceptor levels in Si: we have calculated the B, Al, Ga, In, Tl shallow acceptor energy levels in bulk Si using ab initio method and CPM. 64,000 atom supercells need to be used obtained converged energies. The calculated acceptor levels show the same trend as the experimental results.

Mechanical deformation of CdTe and CdSe tetrapods: we have continued our studies of CdTe and CdSe tetrapods when they are pressed by an AFM tip while sitting on top of a substrate. We find that under the mechanical deformation, the energies of electron states in the tetrapods can cross each other, and the optical spectrum can change significantly. This mechanical-optical coupling can potentially be used in sensors for mechanical stress.

CdTe nanowire higher excited states: in collaboration with experiments in Washington Univ., we have calculated higher excited states and their corresponding optical absorption spectra in CdTe nanowires. This helps to explain the experimentally observed absorption peaks.

Fluorescence resonance energy transfer (FRET) for quantum rods: we have calculated the FRET between quantum rods, and tested the accuracy of the dipole interaction approximations. We found that the error of the dipole interaction is about 10-20% when the two rods are close to each other.

Numerical algorithms: in collaboration with the mathematicians in this project, we have tested different numerical algorithms to solve the interior eigen state problem. We found the Jacobs-Davidson's method can be a few times faster than the conjugated gradient method.

Exciton wavefunctions and binding energies in nanowire: we have constructed variational two body wavefunctions for excitons in nanowires and other nanostructures. We are calculating the exciton binding energies in such structures in order to understand the exciton dissociation problem.

CMOS modeling using linear combination of bulk band (LCBB) method: we have continued our study of using LCBB to simulate nanometered CMOS systems. We have studied individual dopant fluctuation effects and band structure valley coupling effects.

Program Impact:
The development of the charge patching method enables us to calculate thousand atom nanosystems with ab initio accuracy. The calculation is fast and scales linearly to the size of the system.
Interactions:
National Renewable Energy Lab: (A. Zunger). Univ. of Tennessee: (Jack. J. Dongarra).
Personnel Commitments for FY07 to Nearest +/-10%:
Lin-Wang Wang 15%
Joshua Schrier (post-doc) 100%
Authorized Budget (BA):
FY05 $175K FY06 $165K FY07 $165K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020203

FWP and/or subtask Title under FWP: Charge patching method for electronic structures and charge transports of organic and organic/inorganic mixed nanostructures
FWP Number: KC2303

Program Scope: (1) extend and test the charge patching method (CPM) to organic molecules, generate the ab initio electron charge density of these organic molecules without doing direct ab initio calculations; (2) use the folded spectrum method and the single particle Hamiltonian from the patched charge density to study the electronic properties of thousand atom inorganic/organic mixed systems; (3) use CPM in the force field model for the nonbonding interactions for total energy calculations, and develop linear scaling electronic structure calculation methods for organic and organic/inorganic mixed nanostructures.

Major Program Achievements (over duration of 2006 -2007):
The charge patching method for organic molecules: We have generated charge motifs for different types of organic molecules. This includes: alkanes C_nH_{2n+2}; alkenes C_nH_{n+2}; acenes (benzene C_6H_6, naphthalene $C_{10}H_8$, anthracene, tetracene, pentacene); thiophene oligomers $(C_4SH_2)_nH_2$, etc. Charge motifs are generated from small prototype systems, and then used to generate molecule charge densities for much larger molecules and polymers. Van der Waals bonded molecule clusters and stacking are also investigated. Different torsion angle configurations, cis-trans structures are studied. Typically, the electron eigen energies calculated using the charge patching method is within 10-20 meV of the local density approximation (LDA) direct calculated results. Thus, the same motifs can be used to describe the charge density of different torsion angle configurations. Our work proves that the charge patching method can be successfully used to describe the charge density and electronic structures of organic systems.

ZnO (110) surface and organic molecule interface: We have been using ab initio total energy calculation and classic force field method to study the binding of ZnO surface and organic oligomers and polymers. In many cases, the binding between the semiconductor surface and the organic polymers are physisorption. Such binding can be described by force field models with electrostatic charge and van der Waals interactions. We have first used ab initio calculation to study the reconstruction of the ZnO surface, then use force field (FF) to carry out molecular dynamics (MD) simulation for polymers on the ZnO surface. We are currently focused on poly(3-hexylthiophene) (P3HT) oligomer which is used in real solar cell applications. After the MD, we have relaxed the structures to get local minimum atomic configurations using both the FF and ab initio total energy minimization. The final local minimum energy structures of these two methods are compared, and the FF parameters (especially the partial charges) are refitted to yield the ab initio results. The refitted FF parameters are then used for large system and polymer blend MD simulations. The atomic structures of such simulations will be used with the charge patching method and the folded spectrum method to study the electronic structures and charge transports of large organic/inorganic nanocomposite systems.

Linear scaling 3 dimensional fragment method (LS3DF): We have continued to work on the LS3DF method and its code. Now, the LS3DF is a single executable code (instead of series of executables linked by a shell script). The single executable code makes it possible to run it smoothly on the IBM SP machines at NERSC and Cray XT4 machines at NERSC and NCCS. The code scales well up to 8000 processors. It takes about an hour to run a selfconsistent calculation for a few thousand atom system using a few thousand processors. Now, the LS3DF has been used to study internal electric fields and dipole moments of nanocrystals. We plan to use it to study inorganic/organic interface problems in the future. Our LS3DF poster in SC07 conference has been selected as the best poster in that conference.

Program Impact:

The development of charge patching method for organic system allows us to study the electronic structures and charge transports of large polymer, oligomer blends and their nanocomposites with inorganic systems. The development of the LS3DF method allows us to calculate >10,000 atom systems directly.
Interactions:
Personnel Commitments for FY07 to Nearest +/-10%:
Lin-Wang Wang 15%
Nenad Vukmirovic (postdoc): 100%
Sefa Dag (postdoc): 100%
Authorized Budget (BA):

FY05 $0K	FY06 $0K	FY07 $275K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Mechanical and chemical properties of surfaces and interfaces
FWP Number: KC3101

Program Scope:
Fundamental studies of surface structure, friction, lubrication, wear. Energy transfer in nanometer contacts. Atomic scale manipulation. Development of advanced atomic scale imaging and spectroscopy techniques: Scanning Tunneling and Atomic Force Microscopies (STM and AFM), Ambient Pressure Photoelectron Spectroscopy (APPES).

Major Program Achievements (over duration of support):
-Discovered effect of electric fields on binding energy of H on Pd surfaces leading to diffusion and dissolution.
-Discovered enhancement of friction in highly doped semiconductors: p-type Si and n-type GaAs semiconductor during forward bias.
-Discovered unusual friction properties of Al-Ni-Co decagonal quasicrystals: High friction during sliding along periodic direction *vs* sliding along aperiodic direction.
-Molecular manipulation: Determination of mechanisms of manipulation of individual molecules by excitation of single or multiple quanta of vibration and electronic excitations leading to rotation, translation, dissociation. The findings provide deep insights into nature of chemical reactions on surfaces in catalysis
-Discovered water clustering rules in 2 dimensional films on metal surfaces: similar to ice rules but with O bonding to surface through lone pair p-orbital, leading to small islands and second layer growth.
- Determination of the molecular structure of monolayer water films on Ru(0001): intact molecules forming small domains at $T<140K$ and mixed H_2O-OH structures at $T>140K$
-Development of photoelectron spectroscopy under ambient pressure conditions
-Development of Scanning Tunneling Microscopy under ambient pressure conditions
-Development of non-contact AFM techniques for studies of liquid films

Program impact:
Provide fundamental insights into the mechanism of energy dissipation in friction, role of lubricant monolayers under pressure (MEMS, Hard Disk lubes).
Discovery of friction dependence on carrier density on semiconductors (p-Si and n-GaAs) with potential applications of friction control in nanomachines.
Determination of mechanisms of manipulation of single atoms and molecules by elementary excitations (vibration quanta, electronic transitions) impacts catalysis and photochemistry. Opens new possibilities in nanoscience and nanotechnology.
Development of novel instrumentation opens way for fundamental advances in catalysis and environmental sciences

Interactions:
Internal: Molecular Environmental Science at ALS beam line 11. Surface Science and Catalysis (Gabor Somorjai). Molecular Foundry (Alivisatos, Frechet, Bokor, Louie, Bertozzi). External: AMES Laboratory: (tribology of quasicrystals). Sandia Natl. Lab. (Peter Feibelman, theory). Research Council of Spain (STM theory). Ecole Normale Lyon, France (STM theory). Fritz-Haber-Institut Berlin, Germany. University of Paris-VI: *ab-initio* calculations of chemisorption.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Oustanding Perfomance Award (LBL). Klaus Halbach Award for development of Innovative Instrumentation. Distinguished Lecturer of "Frontiers in Chemical Research" at Texas A & M University. Conference Speaker at dedication ceremony of new High Pressure beam line of German Synchrotron facility (BESSY)

Personnel Commitments for FY07 to Nearest +/- 10%:
Staff: M. Salmeron (10%), Postdocs: Franck Rose (100%), Sabine Maier (100%). Students: Mousslim Tatarkhanov (25%), Yabing Qi (25%), Ingeborg Stass (100%), Admin: Alice Muller-Egan (50%)

Authorized Budget (BA):

FY05 $405K	FY06 $405K	FY07 $525K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Surface Science and Applications Program
FWP Number: KC3102

Program Scope:
The structure and composition of solid surfaces (metal single crystals, nanoparticle and polymer films) and adsorbed monolayers are determined on the atomic scale with continually increasing spatial and time resolution. Metal nanocrystals in the 1-10 nm range and controlled shape are synthesized and assembled as monolayer films. STM, AFM, and SFG techniques are utilized in most of these studies applied at high pressures (atm) and at liquid interfaces. The rate and selectivity of catalyzed surface reactions are studied using single crystal surfaces and nanoparticles, *in situ*, and correlated with surface structure size and composition. Instruments have been built that permit molecular level surface studies from high pressures to ultra high vacuum, over fourteen orders of magnitude pressure range using SFG-surface vibrational spectroscopy, STM and AFM. Adsorption and surface structure of amino acids peptides are studied on hydrophobic and hydrophilic surfaces by SFG. For the first time, the atomic level surface properties can be studied <u>during adsorption and during chemical reactions at high pressures</u> and temperatures and at solid-liquid interfaces.

Major Program Achievements (over duration of support):
Reaction studies on platinum and rhodium single crystal surfaces using SFG have been extended to Pt, Rh and bimetallic nanocrystals. Platinum and rhodium nanoparticle monolayer films could be monitored by sum frequency generation (SFG) – vibrational spectroscopy in a prism geometry which is much more sensitive to nanoparticle assembly than slab geometry. The polymer cap that encapsulates the metal nanocrystals is porous to molecules that adsorb on the metal nanoparticle surfaces. Therefore, we could extend our adsorption and catalytic reaction studies by SFG from single crystals to nanoparticle films. The selectivity of multipath catalytic reactions depends on both size and shape of nanoparticles. Platinum/rhodium bimetallic nanoparticles, over a wide range of compositions but the same 9 nm size, have been synthesized. Since the CO oxidation rate is 20 times faster on rhodium, the bimetallic system permits tuning of the reaction rate by varying the composition over a wide range. Adsorption of amino acids and peptides reveals changes of structure on hydrophobic and hydrophilic interfaces in water solution detected by SFG.

Program impact:
Determined the molecular and structural properties that influence surface chemical reactivity of metal crystal and nanoparticle surfaces; the mobility of surface atoms and adsorbed molecules, and the metal surface structure. Changes of bonding of peptides on hydrophobic and hydrophilic surfaces were detected.

Interactions:.
Polymer Technology Group, Berkeley CA; Qualcom, Inc., San Jose, CA; Intel Corp., Santa Clara, CA; University of California, Berkeley: Prof. Jeff Bokor, Electrical Engineering; Prof. Kyriakos Komvopoulos, Mechanical Engineering; Prof. Song Li, Bioengineering and Prof. Peidong Yang and Professor Paul Alivisatos, Chemistry.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2008 Priestley Medal from the American Chemical Society, <u>Docteur Honoris Causa</u>, Inst. of Chemistry, Chinese Academy of Sciences, Molecular Science Forum Lectureship, Center for Molecular Science, Chinese Chemical Society
30 invited talks since January 2006

Personnel Commitments for FY07 to Nearest +/- 10%: Gabor **Somorjai** (PI) 20%
Feng Tao (post-doc) 100%; Cesar Aliaga (post-doc) 100%; Derek Butcher, Chris Kliewer, George Holinga and Jamie Kulp (students) 50%, Inger Coble (Administrator) 75%

Authorized Budget (BA):
FY05 $740K FY06 $740K FY07 $740K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Microscopy Investigations of Quantum Dots, Nanorods, and Soft Condensed Matter
FWP Number: KC3103

Program Scope:
This program develops state-of-the-art of optical characterization microscopies, such as single quantum dot intermittency dynamics, broadband CARS microscopy, apertureless NSOM (ANSOM), and femtosecond pump-optical injection probing spectroscopies of single nanostructure species under stimulated emission conditions. The methods are used in particular to address applications in solar energy. A parallel molecular beam epitaxy growth effort for processing semiconductor materials with in situ scanning tunneling microscopy is used to study the growth mechanisms of III-V nitrides and doped nitrides. Development of novel microscopies provide new spectral and spatial windows into the analysis of materials for DOE missions in energy utilization.

Major Program Achievements (over duration of support):
Growth studies of flat InGaN and InGaN doped with Pr have been performed. The kinetics of energy transfer from the InGaN to Pr as a function of band gap has been measured. Apertureless near field microscopy studies of GaN and InN islands have revealed contrast mechanisms due to the real and imaginary parts of the index of refraction, measuring nanometer size Ga metal islands, and probing InGaN islands. Results show contrast mechanisms due to changes in stoichimetry and size of the islands, which has been modeled in detail. The full electric field, including phase, has been analyzed around gold nanoparticles. Ultrafast laser, differential gain experiments on ZnO lasing in nanowires and tetrapods have been performed to measure the timescales and ratios of electron-hole plasma and exciton mechanisms during lasing in nanostructured materials. Using upconversion methods, the wavelength and time dependences of the lasing pulses from individual nanowires are measured. A single pulse CARS microscopy project using an ultrafast laser with interferometric detection produces complete Raman spectra while spatially scanning. Polymer domains have been analyzed with vibrational spectral sensitivity, and new work is cross linking of hydrogen silsesquioxane. CdSe quantum dot and rod fluorescence intermittency is studied with isolated single dot specificity, showing a significant wavelength dependence with greatly increased "off" times at shorter excitation wavelengths.

Program Impact:
New forms of microscopy with chemical and single nanostructure specificity and the study of mechanisms of excitation and flow of energy have significant impact on DOE's mission in energy conversion and utilization. Studies of InGaN and alloyed nitrides are important for the lighting industry and for solar conversion efficiency.

Interactions:
A collaboration with ALS and Molecular Foundry scientists involves the studies of quantum dot intermittency, antenna field enhancement, and polymer cross linking.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Invited Speaker at American Chemical Society Boston National Meeting. Keynote speaker at the University of Tennessee Frontiers in Chemical Physics Symposium.

Personnel Commitments for FY07 to Nearest +/- 10%:
S. Leone (PI) 5%, A. Tivanski (postdoc) 20%, L. Kranz (visiting student) 50%, A. Caster (graduate student) 10%, A. Schwartzberg (postdoc) 100%, K. Knappenberger (postdoc) 10%, Y. Abate (postdoc) 50%, A. Caughey (graduate student) 20%.

Authorized Budget (BA):
FY05 $390K FY06 $390K FY07 $390K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP Self-assembly of organic/inorganic nanocomposite materials
FWP #: KC3104
Program Scope: Create functional materials by parallel and hierarchical self-assembly. Develop wet chemical processes by which organic/inorganic composites can be created with a high degree of control on many length scales simultaneously. By developing a comprehensive ability to pattern organic/inorganic composites, it will be possible to design complex materials in which several microscopic processes are independently and simultaneously optimized. Target functional materials with applications in energy conversion, mechanical composites, and optical/electrical devices. The team: Paul Alivisatos (Nanocrystals); Jean Frechet (Organic Components); Miquel Salmeron (Imaging) ; P. Yang (Nanowires), Lin Wang Wang (Theory); A. Zettl (Nanotubes-proposed to be added) .
Major Program Achievements (over duration of support): Demonstrated the concept of hybrid inorganic-organic nanorod – polymer solar cells (Science 2002, *295*, 2425.); developed dual nanocrystal solar cell (Science 2005); General route to vertical ZnO nanowire arrays using textured ZnO seeds (Nano Lett 2005); Nanowire dye-sensitized solar cells (Nature Materials, 2005); developed new specialty electro-active surfactants that solubilize inorganic nanorods, while permitting electron transfer (Adv. Mat. 2002); calculated the energy levels of semiconductor nanorods vs. aspect ratio, and verified the prediction that the degree of polarization should change dramatically at aspect ratio of 2 (Science 2001, *293*, 1455, Journal of Physical Chemistry B 2002, *106*, 2447); discovered the existence of liquid crystal phases of inorganic semiconductor nanorods (Nano Letters 2002, *2*, 557.). Computed the energy levels of exotically shaped nanocrystals – arrows and teardrops (Nano Letters 2003); demonstrated the synthesis in high yield of branched nanocrystals(Nature materials 2003) and hyper-branched nanocrystals (Nano Letters, 2005); demonstrated the growth of nanocrystals by microfluidic techniques (Nano letters 2003, JACS 2005); demonstrated solution phase X-ray absorption spectroscopy of Co nanocrystals; Electrical and AFM investigations of individual inorganic tetrapods.
Program Impact: Examples of Applications: hybrid nanorod – polymer solar cells; light emitting diodes; mechanical reinforcement of plastics. Education: About 300 scientists have been trained in the combined labs, and are now active in the science community. (alumni at Univ. of Tokyo, DuPont, Rohm & Haas, Univ. Lausanne, Northwestern Univ., Stanford Univ., Univ. Arkansas, Cambridge University, Harvard, Hebrew Univ. of Jerusalem, Intel, Univ. of Mainz, MIT Media Lab, Mitsubishi Chemical, Nanosys, Quantum Dot Corp., Rice, National Taiwan University, Siemens, UCLA, Vanderbilt). Patents: Ten issued. Founded two companies: Quantum Dot Corp. (fifty employees) with focus on biomedical applications of semiconductor nanocrystals, and Nanosys, Inc., with focus on electro-optic applications. Press Articles: C&E News, Science, Nature, Science News, Scientific American, MIT Technology Review, Red Herring, Business Week Service to the community: Founding editor-in-chief of Nano Letters (American Chemical Society); **Interactions:** Current team members: Paul Alivisatos (Chemistry and MSD) Jean Frechet (Chemistry and MSD), Miquel Salmeron (MSD); Lin Wang Wang (NERSC); Collaborators: Richard Mathies (Chemistry) (Daniel Chemla (Physics and MSD), Alex Pines (MSD and Chemistry), Anupam Mahukar (USC), Ned Seeman (NYU), Laura Landweber (Princeton), Priya Vashista (LSU), Lydia Sohn (Princeton). Former collaborators: Chuck Shank, Peter Schultz, Paul McEuen. Industry Interactions: 3M, Dow Chemical, Dupont, Intel, Kodak, Motorola, Xerox; Bayer, BASF, Mitsubishi Chemical, Samsung.
Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): Alivisatos: ~30 invited lectures/year including 4 plenary/endowed lectures in the past year; Ernest Orlando Lawrence Award; Eni Italgas Prize for Energy and Environment; Colloid and Surface Chemistry ACS Award; NAS, Amer. Acad. of Arts and Sciences, Tech Transfer Award (LBNL); Larry and Diane Bock Chair in Nanotechnology, Univ. of Chicago Distinguished Alumni Award, Rank Prize for Optoelectronics; Miller Research Professor; Chancellor's Professor. **Fréchet**: NAS, NAE, AAAS; ACS Award in Polymer Chemistry, Butler Lecturer Florida, ACS Salute to Excellence Award, ACS Cope Scholar Award, Baker Lecturer Cornell, Stauffer Lecturer Stanford, Bayer Lecturer, Pittsburgh, Chute Lecturer Dalhousie, Merk-Frosst Lecturer Alberta, Chambers Lecturer Rochester, Dow Karabatos Lecturer Michigan State, Doctorate (Honoris Causa) Universite Claude Bernard, France. **Salmeron**: Outstanding Performance Award, LBNL (2007 & 2001); Klaus Halbach Award for Development of Innovative Instrumentation; Elected Fellow of the American Vacuum Society; Plenary lecturer 18th European Conf. on Surface Science, Keynote speaker 1st Latin American Sym. on Scanning Probe Microscopy. **Yang**: NSF A.T. Waterman Award; Molecular Science Forum Professorship, Chinese Academy of Science, McElvain Lectureship, Univ. of Wisconsin; ACS Pure Chemistry Award; Camille Dreyfus Teacher-Scholar Award. **Zettl**: Miller Professorship; James C. McGroddy Prize for New Materials; LBNL Outstanding Performance Award (2004).
Personnel Commitments for FY07 to Nearest +/-10%: P. **Alivisatos** (PI), M. Salmeron (senior scientist) 10%, D.F. Ogletree (staff scientist) 10%, 12 100% graduate students, 8 100% postdoctoral fellows, 2 visitors.
Authorized Budget (BA):
FY05 BA $1253K FY06 $1253K FY05 $1253K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Physical Chemistry of Nanocrystals
FWP Number: KC3105
Program Scope: Nanometer size inorganic crystals are playing an increasingly important role in solid-state physics, chemistry, materials science, and even biology. Many fundamental properties of a crystal (e.g., ionization potential, melting point, band gap, saturation magnetization) depend upon the solid being periodic over a particular length scale, typically in the nm regime. By precisely controlling the size and surface of a nanocrystal, its properties can be tuned. Using techniques of molecular assembly, new nanocrystal-based materials can in turn be created. This program encompasses fundamental studies of the mechanisms and kinetics of nanocrystal synthesis as well as studies of scaling laws for optical, electrical, magnetic, and structural size dependent properties.
Major Program Achievements (over duration of support): Helped develop the concept of inorganic nanocrystals as a class of macromolecule. First studies of surface derivitization and isolation of nanocrystals, and immobilization of nanocrystals on self-assembled monolayers; first photoelectron spectroscopy studies of nanocrystal electronic structure (with Jim Tobin) and nanocrystal surface structure. X-ray Absorption Spectroscopy as a tool for determining nanocrystal surface structure; first measurements of single nanocrystal x-ray absorption spectra. Synthesis and shape control of semiconductor nanocrystals and nanorods of CdSe, InP, InAs, GaAs, Co, and Fe_2O_3. Discovery of branching in nanorod synthesis of II-VI semiconductors, including synthesis of tetrapods and inorganic dendrimers. Studies of core-shell nanocrystal synthesis and properties. Optical properties of nanocrystals, including hole-burning, resonance Raman, photon echo, Stark effect; polarization and blinking studies of quantum dots and nanorods. Studies of pressure and temperature induced structural transformations in nanocrystals. Single nucleation events in nanocrystal structural transformations; shape change as an indicator of mechanism in nanocrystal transformations, first measurements of activation energy and activation volume in nanocrystal structural transformations. Hollow nanocrystal formation through the nanoscale Kirkendall effect. Cation exchange kinetics, reversibility, mechanism in nanocrystals. First electrical device based on a nanocrystal-polymer composite (light emitting diode); first transistor based on a single nanocrystal and a single molecule (with Paul McEuen); developed the use of DNA as a tool for patterning nanocrystals (with Peter Schultz); discovered liquid crystal phases of semiconductor nanorods; introduced the use of colloidal quantum dots as fluorescent biological labels (with Shimon Weiss); first demonstrated the plasmon spectroscopic ruler for measuring nanoscale distances. Hybrid nanorod-polymer solar cell. Dual Nanocrystal Solar cell
Program impact: Light emitting diodes, solar cells, solar concentrators, fluorescent biological labels (reduced photobleaching, multiplexed assays), magnetic storage, magnetic bio-labeling, mechanical reinforcement of composites. Education: About 75 scientists have been trained in the lab, and are now active in the science community. (alumni at Stanford, Columbia Univ., Depart. of State-Washington D.C., Exxon-Mobil, General Electric, Harvard, Hebrew Univ. of Jerusalem, IBM-Almaden, Indiana Univ., Intel, MIT, Mitsubishi Chemical, Nanotero, Nanosys, Inc., National Nanotechnology Lab- Italy, Quantum Dot Corp., Rice, National Taiwan University, Seeo, Inc., Stanford, Texas A&M, Univ. of Arkansas, Univ. of Cambridge, Univ. of Munich, Univ. of Hamburg, Univ. of Cagliari-Monserrato Italy, UCR, UCSF, UCLA, Vanderbilt, Virginia Tech).
Interactions: Current collaborators: Jan Liphardt (Physics and PBD), Phil Geissler (Chemistry and PBD), Jean Frechet (Chemistry and MSD), Daniel Chemla (Physics and MSD), Alex Pines (MSD and Chemistry), Anupam Mahukar (USC), Ned Seeman (NYU), Priya Vashista (LSU), Wendell Lim (UCSF); Former collaborators: Chuck Shank, Peter Schultz, Paul McEuen. Industry Interactions: Founder, Quantum Dot Corporation; Founder, Nanosys, Inc.
Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): Patents: Ten issued. Founded three companies: Quantum Dot Corp., now acquired by Invitrogen, biomedical applications of semiconductor nanocrystals; Nanosys, Inc. electro-optic applications of nanocrystals; Solexant, Inc. , solar cells based on nanocrystals. Small Times 2003 Researcher of the Year. 2nd most cited scientist in nanotechnology for 1993-2003 (ISI). Press Articles**:** C&E News, Science, Nature, Science News, Scientific American, MIT Technology Review, Red Herring, Business Week, Service to the community: Founding editor, Nano Letters (ACS); past Associate Editor, Ann. Rev. of Phys.Chem.; co-author with Mike Roco (NSF) and Stan Williams (HP) of the National Nanotechnology Initiative Report. Awards: ~30 invited lectures/year including 4 plenary/endowed lectures in the past year; Ernest Orlando Lawrence Award; Eni Italgas Prize for Energy and Environment (with Alan Heeger); Colloid and Surface Chemistry ACS Award; NAS, Amer. Acad. of Arts and Sciences, Tech Transfer Award (LBNL); Larry and Diane Bock Chair in Nanotechnology, Univ. of Chicago Distinguished Alumni Award, Rank Prize for Optoelectronics; Larry and Diane Bock Professor of Nanotechnology; Miller Research Professor; Chancellor's Professor. **Personnel Commitments FY207:** A.P. **Alivisatos**-PI (10%), 3 100% graduate students, 1 100% postdoctoral, 1 50% postdoctoral, 1 16% postdoctoral visitors.
Authorized Budget (BA):

FY05 $615K	FY06 $615K	FY07 $615K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Multi-component assembly of high surface-area ordered oxide-metal nanocomposites with enhanced catalytic properties.
FWP Number: KC3106

Program Scope: Developing novel synthetic strategies for shape-controlled growth of Pt, Pd and bimetallic nanocrystals, ideally with one type of surface exposed only; 2-dimensional assembly of these nanocrystals using Langmuir-Blodgett technique; 2- and 3-dimensional Assembly of these shaped nanocrystals within ordered porous oxide (SiO_2, Al_2O_3, TiO_2) matrix; Chemical reaction testing on the ordered metal-oxide nanocomposites to examine the effect of surface type of the nanocrystals, interface and surface area on the catalytic activity and selectivity.

Major Program Achievements (over duration of support):
(1). Cubic, cuboctahedral, and porous Pt nanoparticles were prepared using tetradecyltrimethylammonium bromide as a surface stabilizing reagent. The nanoparticles which are electrostatically capped with alkylammonium ions and shape-controlled without aid of foreign metal ions show superior catalytic activity in comparison to nanoparticles prepared with a polymeric stabilizing reagent and silver. At 100^{o}C, C_{14}TABr-capped cubes were ~10 times more active than PVP-capped cubes.

(2). Benzene hydrogenation was investigated for different shapes, cubic and cuboctahedral Pt nanoparticles in the presence of a surface monolayer consisting of tetradecyltrimethylammonium bromide (C_{14}TABr). Infrared spectroscopy suggests that C_{14}TABr binds to platinum through a weak C-H···Pt bond of the alkyl chain to the platinum surface. The catalytic selectivity was found to be strongly affected by the nanoparticle shape. Both cyclohexane and cyclohexene product molecules were formed on cuboctahedra nanoparticles whereas only cyclohexane was produced on cubic particles. These results are similar to the product selectivities obtained by the previous studies on Pt(111) and Pt(100) single crystals. The apparent activation energy for cyclohexane production on the cubic nanoparticles is 10.9 ± 0.4 kcal/mol. For cuboctahedral nanoparticles, the apparent activation energies for cyclohexane and cyclohexene production are 8.3 ± 0.2 kcal/mol and 12.2 ± 0.4 kcal/mol, respectively. Comparing to previous studies on platinum single crystals, the activation energies for nanoparticles are lower than their single crystal surface counterpart. Conversely, the turnover rate (TOR) of benzene hydrogenation on the nanoparticle is *three times* higher than on the platinum single crystal surfaces.

(3). Nanocrystal shape control for both single and multiple material systems remains fairly empirical and challenging. New methods need to be explored for the rational synthetic design of heterostructures with controlled morphology. Overgrowth of a different material on well-faceted seeds, for example, allows for the use of the defined seed morphology to control nucleation and growth of the secondary structure. Recently, we have used highly faceted cubic Pt seeds to direct the epitaxial overgrowth of a secondary metal. We demonstrated this concept with lattice matched Pd to produce conformal shape-controlled core-shell particles. Seeding with faceted nanocrystals may have significant potential towards the development of shape-controlled heterostructures with defined interfaces.

Program Impact:
Enabling the deterministic assembly of high surface-area oxide-metal nanocomposites with enhanced catalytic activity and selectivity (i.e. catalyst-by-design).

Interactions:
G. Somorjai (Chemistry): Catalytic reaction studies on the high surface-area ordered metal-oxide nanocomposites.

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

2007	Max Planck Lectureship, Max Planck Institute, Stuttgart, Germany
2007	NSF Alan T. Waterman Award.

Personnel Commitments for FY07 to Nearest +/-10%:
P.D. **Yang** (PI) 20%**;** H. Lee (postdoc) 100%; Susan Habas (graduate Student) 100%

Authorized Budget (BA):
FY05 $195K FY06 $195K FY07 $195K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Nuclear Magnetic Resonance
FWP Number: KC3107
Program Scope: The nuclear magnetic resonance (NMR) program has two complementary components. The first is the establishment of new concepts and techniques in NMR and its offspring, magnetic resonance imaging (MRI), in order to extend their applicability and enhance their capability to investigate molecular structure and organization from materials to organisms. The study and diagnostic use of nuclear spins interacting with each other and with others degrees of freedom requires the development of new theoretical and experimental methods; one consequence of these efforts is the design and fabrication of next-generation NMR and MRI equipment. The second component of the research program involves the application of such novel methods, together with other programs, and with outside laboratories and industry, to significant problems in chemistry, materials science, and biomedicine. It is the unique environment of interdisciplinary research and large-scale instrumentation capabilities at the Lawrence Berkeley National Laboratory that cultivates these innovations, their diverse applications, and technology transfer.

Major Program Achievements (over duration of support): Some principal developments: Helped launch high-resolution solid-state now widely used in materials, chemistry and biology; introduced multiple-quantum spectroscopy; developed zero-field Fourier-transform NMR using both field cycling and superconducting detectors; introduced dynamic-angle spinning and double rotation for quadrupolar nuclei such as oxygen-17 and aluminum-27; made advances in optically pumped and detected NMR and MRI, and the development of novel xenon and para-hydrogen-based highly polarized NMR molecular sensors; introduced ex-situ scanning, remote detection, and ultralow and zero-field SQUID and laser magnetometer detection of NMR and MRI, opening the way to in-the-field observation of objects and subjects not amenable to normal methods of NMR and MRI. Examples of applications: flow, mixing , and dispersion of fluids in porous materials, microfluidic NMR and MRI "lab on a chip," studies of structure and dynamics in minerals and oil reserves, molecular assays, catalysts, semiconductors, surfaces, amorphous materials, quantum dots, polymers and dendrimers, biomolecules, biosensors, tissue, organisms, diagnostic biomedical molecular imaging.

Program impact: "Seeing is believing" novel techniques and devices of magnetic resonance spectroscopy and imaging have expanded our ability to "see" into materials and organisms. The concepts and instrumentation, adopted worldwide by laboratories and industry, are being used to investigate molecular structure and organization from the nanoscale dimensions of catalysts and polymers to the macroscopic proportions of human imaging and oil exploration. Education: hundreds of scientists ("Pinenuts") trained in the laboratory, many holding leading positions in academia and industry. Patents: more than twenty issued, filed, pending or disclosed methodologies licensed, adapted into commercial NMR technology. Journal Covers and News Recognition: eg Nature, Nature Materials, Nature "News and Views", Science, Science "Perspectives", Technology Review, Photonics.com, New ScientistTech, Spectroscopy, J. Mag. Resonance, Angewandte Chemie, J. Physical Chemistry, C&E News, Science News, Biophotonics, Analytical Chemistry, R&D Magazine., PNAS "Commentary", Physics World.

Current Interactions: D. Wemmer (Physical Biosciences and Chemistry), J. Clarke (MSD and Physics), D. Budker (NSD and Physics), T. Budinger and S. Conolly (LSD and Bioengineering), M. Francis (MSD and Chemistry). Industry: eg Schlumberger-Doll Research, Chevron, Varian, General Electric.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): e.g. Glenn T. Seaborg Chair, UC Berkeley; Docteur Honoris Causa Universities of Rome and Paris: Member, National Academy of Sciences; DOE E.O. Lawrence Award; Wolf Prize in Chemistry; Centenary Medal, Royal Society of Chemistry; ACS Irving Langmuir Award; ACS F.A.Cotton Medal; Tetelman Fellow, Yale U; Ampere Congress Honoring AP's 50'th Birthday; R&D-100 Awards 1987, 1989; Univ Calif Distinguished Teaching Award; *Lectureships including:* Professeur Joliot-Curie; Ecole Superieure Phys Chem, Paris; Loeb Lecturer, Harvard U; Lord Lecturer, MIT; Roberts Lecturer, Caltech; Hinshelwood Professor, Oxford U; Lord Todd Professor, Cambridge U; Faraday Medal, Royal Society; Seaborg Medal, UCLA; Scientific American "50 Visionaries;" Elected Foreign Member, Royal Society (London): 60th Birthday International Ampere Symposium in Honor of Alex Pines, Chamonix France (2005); Medal of the NMR Society of Japan (2005); Distinguished Visiting Professor several Institutions (2006); new patents (2007); R&D 100 Award: Laser Detected MRI (2007).
Web Pages: http://waugh.cchem.berkeley.edu/research/ http://waugh.cchem.berkeley.edu/alex/

Personnel Commitments for FY07: A. **Pines** PI 25%, 16 graduate students, 6 postdoctoral fellows.
Authorized Budget (BA):
FY05 $872K FY06 $872K FY07 $1000K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Plastic Electronics
FWP Number: KC3108
Program Scope:
This program is aimed at the development of the fundamental understanding of the molecular and physical principles that govern the design of novel materials for organic or plastic electronics. The program aims at the exploration of newly designed materials, the determination of their physical and functional properties, and the comparison of these properties with those of known materials to provide access to a better understanding of the design rules and structure-property relationships for this important family of energy related materials. Based on novel design concepts the synthesis of new organic molecules, oligomers and polymers with interesting electrical and optical properties will be explored and studied. Experimental methods for the control of microstructure and morphology, particularly in thin films will be developed with the aid of scattering and a variety of microscopy tools including atomic force microscopy and transmission electron microscopy. As part of a feed-back loop, the newly designed materials undergo functional testing in model devices: transistors, light emitting diodes, photovoltaics, etc.
Major Program Achievements (over duration of support): Development of electroactive oligomers capable of self-assembly into ordered monolayers transistors (Subramanian-Frechet). Design and study of monolayer transistors based on self-assembling multifunctional macromolecules (Subramanian). Development of novel bipolar electroactive copolymers for highly efficient solution cast-light emitting diodes. Study of the effect of architecture and composition on the self-assembly of functional polymers into phase separated structures that achieve optimal electronic properties. Study of sophisticated unsymmetrical or dendronized structures involving energy transfer between active moieties to maximize device performance. Exploration of the functionalization of carbon nanotubes for application in organic photovoltaic devices (Frechet). Development of a platform of self-assembling, conjugated block polymers and developed magnetic field alignment to gain nanostructural control (Segalman). Probed the effects of controlled nanostructure on plastic light emitting diodes and photovoltaics (Segalman-Frechet). Developed an entirely new application of organic semiconductors (thermoelectrics) and used these devices to gain fundamental insight to charge transport (Segalman).
Program impact: Inexpensive/energy efficient printed electronic devices, efficient solid state lighting, efficient and low-cost harvesting of solar energy, flexible photovoiltaics. Given the importance of electroactive polymers and oligomers in energy related issues it is important to gain a fundamental understanding of structure-function relationships. While the discovery of novel, better performing and energy efficient materials is a key target, we also focus on critical issues such as the control of their self-assembly into ordered structures that maximize energy efficiency; the study of factors that contribute to self-ordering and ultimate device performance, and the development of methods for optimal device construction. This program is highly interactive and multidisciplinary.
Interactions:
Paul Alivisatos, Nitash Balsara, Jeff Kortright, Arun Majumdar, Howard Padmore, A. Zettl, M. Crommie (All UC Berkeley) G. Hadziioannou (Strasbourg), V. Ganesan (UT Austin), M. Thompson (USC); M McGehee (Stanford), Intel, X. Li (Advanced Photon Source), E.L. Thomas (MIT), J. Luning and M. Toney (Stanford Synchrotron)

Recognitions, Honors and Awards: ***Segalman***: MDV Innovators Award; Hellman Family Young Faculty Award; 3M Untenured Faculty Award; NSF-CAREER Award; Intel Young Faculty Seed Grant Award, Chateaubriand Fellowship. ***Frechet***: National Academy of Sciences, National Academy of Engineering, American Academy of Arts and Sciences, 2007 A.C. Cope award for outstanding achievement in Organic Chemistry; 2006 Macro Group UK Medal (joint Royal Society for Chemistry and Society of Chemical Industry) for Outstanding Achievement in Macromolecular Chemistry. 2005 Esselen Award for Chemistry at the Service of the Public; 2005 Chemical Communications Anniversary Award; Fellow AAAS; ACSAward in Polymer Chemistry 2000, ACS Salute to Excellence Award 2001, ACS Cope Scholar Award 2001, ACS Award in Applied Polymer Science. *Numerous other awards and lecture series including* Baker Lecturer-Cornell, Stauffer Lecturer- Stanford, Dupont Lecturer-U Penn, Gassman Lecturer-U Minn. ***Subramanian**:* NSF Young Investigator, TR100 innovator

Personnel Commitments for FY07 to Nearest +/- 10%:
J. Frechet 10% (PI, program leader), R. Segalman 10% (co-PI), V. Subramanian 10% (co-PI); C. Zonte (student, 50%) B. Ma (postdoc 100%), D. Poulsen (student 50%); K. Puntambekar, (Postdoc, 100%); J. Lee, (student, 50%); B. Mattis, (student, 50%); Y. Tao (Student, 50%), Y.R. Hong (Student 50%%) S.Y. Jang (Student 50%) B. Thompson (postdoc 100%). Claire Woo (student 50%), Clayton Mauldin (student 50%) Tabitha Clem (st 50%)
Authorized Budget (BA)
FY05 $861K FY06 $861K FY07 $861K

Laboratory Name: Lawrence Berkeley National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP: Biomolecular Materials Program
FWP Number: KC3109
Program Scope: Mimicking or application of biological materials and processes in the materials sciences. Mimicking of membranes and membrane receptors for coatings and functional interactions with living cells; of carbohydrates for controlled interface properties; of proteins for nanoscale conducting wires and self-assembling building blocks for functional assemblies; of DNA and dendrimers for 3-D patterning of inorganic nanocrystals, and as components of functional assemblies. Theory support for experimental work.
Major Program Achievements (over duration of support): Biosensors that turn color in the presence of agents such as influenza virus, botulinum toxin (*Bednarski/Charych*). Development of ultrasensitive SQUID based biosensors for pathogens (*Alper/Clarke*). Polymers that significantly improve the stability of proteins in unbuffered solutions and at elevated temperatures (*Bednarski*). Development of catalytic antibodies. Systems to insert non-natural amino acids into proteins (*Schultz*). The effect of specific amino acid substitutions on proteins temperature stability (*Kirsch*). Enzyme mechanisms for discrimination between optical isomers (*Koshland*). Methods for interfacing biological materials with synthetic materials. New approach for modifying carbon nanotubes with biocompatible coatings. Development of a nanoinjector for penetrating cell membranes with cargo. Method for bottom-up synthesis of carbon nanotubes (*Bertozzi*). Methods for isolating gold nanocrystals bearing discrete numbers of DNA oligonucleotides and the preparation of dimers and trimers of these DNA-nanocrystal assemblies and a wide variety of other spatial arrangements of nanocrystals. Discrete quantum dot Au assemblies and Au nanocrystal spectroscopic plasmon ruler (*Alivisatos*). A series of unnatural building blocks to enable automated preparation of self-assembling dendritic materials based on DNA base pairing. Preparation of dendritic “nanoreactors” that mimic the catalytic function of enzymes effecting both catalysis and transport in solution (*Fréchet*). Well defined assemblies of nanocrystals in specific arrangements (*Fréchet/Alivisatos*). Attachment of polymers and other molecules to the viral coat protein as building blocks for complex structures. Functionalization of tobacco mosaic virus coat proteins to allow the construction of linear artificial light harvesting systems. Chemical modification of spherical viral capsids to provide versatile platforms for diagnostic imaging. Efficient chemical strategies for the modification of protein building blocks, including the attachment of DNA strands to facilitate integration with nanoparticles and other surfaces (*Francis*). A system to deliver biological molecules to prepatterned membrane structures using targeted membrane fusion. Activation of neurons from synthetic supported membranes and use of nanopatterned hybrid inorganic/organic membrane interfaces to repattern a synapse with a living Tcell. Application of *in situ* photolithographic patterning technology to membrane patterning on colloidal particles. Use of membrane coated colloidal particles as sensitive detection assay. Broadly scalable strategy for constructing synthetic cell membrane surfaces displaying natural cell surface proteins with genetically encoded fluorescent markers (*Groves*).
Program Impact: Biosensors for study by industry/government for military/civilian use. Expanded capability to modify enzymes for novel functions. Commercial product for stabilization of proteins at high temperatures and in unbuffered solutions. Techniques for creating hybrid devices of living cells and non-living materials, and for integrating nanoscale materials into biological systems. Over 10 papers/year in major peer reviewed journals.
Interactions: C. Larabell, UCSF; L. Landweber, Princeton; N. Seeman, NYU; M. Dustin, NYU; M. Callstrom, Ohio State; A. Tomsia*C.B.*, R. Ritchie, K. Healy, R. Mathies, E. Isacoff, LBL and UCB; A. Zettl (LBNL/UCB)*C.B.*, Arto Nurmikko (Brown), Harry Atwater (CalTech), Angela Belcher (MIT), Rajesh Naik (AFRL), Johnathon Trent (NASA), Chad Paavola (NASA). Colin Nuckolls (Columbia), Ken Raymond (UCB), Graham Fleming (UCB), Jim O'Neil (LBNL). **Other collaborators:** Rich Mathies (LBNL)*C.B.*
Recognition, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Bertozzi-Ernst Scvhering Prize, Whistler Award, Gibbs Award (ACS), Elected National Acad. Sci., Amer. Acad. Arts & Sciences, Irving Sigal Young Invest. Award-Protein Society, ACS Award-Pure Chemistry, Merck Academic Development Award, Pres. Early Career Award-Science & Engineering, MacArthur Found. Award, Camille Dreyfus Teacher-Scholar Award, Arthur Cope Scholar Award ACS. *Alivisatos*-Nat. Acad. Sci. Amer. Acad Arts and Sci. ACS Colloid and Surf. Sci. Award. Fellow, AAAS, APS, Wilson Prize-Harvard, Coblentz Award, Sloan Found. Fellow, Pres.Young Investigator, Outstanding Young Invest.-MRS, Editor-in-Chief NanoLetters, Associate Ed. Ann Rev Phys Chem, Editorial Board: J Phys Chem, Chem Phys, J Chem Phys. *Fréchet*-Nat. Acad Sci, Nat Acad Engin, Amer Acad Arts Sci, ACS Award-Polymer Chem, 2007 AC Cope Award for outstanding achievement in organic chemistry, 2006 Macro Group UK Medal (Royal Society for Chemistry and Society of Chemical Industry) for Outstanding Achievement in Macromolecular Chemistry, 2005 Esselen Award for Chemistry in the service to the public, ACS Salute to Excellence Award, ACS Award in Polymer Chemistry, ACS award in Applied Polymer Science, ACS Cope Scholar Award, Baker Lecturer-Cornell, Stauffer Lecturer- Stanford, Dupont Lecturer-U Penn, Gassman Lecturer-U Minn. *Groves*- Searle Scholars Award, MIT TR100 (2003), Beckman Young Investigator Award (2004), ACS Langmuir Lecture Award (2005). *Francis*-Hellman Faculty Award (2004) Dreyfus Foundation Award, NSF Career Award (2004), GlaxoSmithKlein Award (2006), Noyce Prize for Excellence in Undergraduate Teaching (2006).
Personnel Commitments for FY07 to Nearest +/-10%: Profs. M. **Alper**, P. Alivisatos, J. Fréchet, P. Geissler, J. Groves, M. Francis, and C. Bertozzi at 10%. 5 post-docs at 100%, 5 GSRAs at 100%.
Authorized budget (BA):

FY05 $732K	FY06 $732K	FY07 $732K