Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0201010, KC0202030, KC020601

FWP: Theoretical Studies of Metals, Alloys, and Ceramics

FWP Number: ERKCM01

Program Scope: First principles theory is used to predict materials properties, relate them to the electronic structure, provide fundamental insights, and guide experimental programs in alloy and ceramic development and nanoscience. Molecular dynamics, based on first principles derived potentials, is used to study the influence of nanoscale defects on macroscopic properties. Global optimization and parallel algorithms are used to extend the applicability of first principles approaches to experimentally relevant nanostructures.

Major Program Achievements: Pioneered development of first principles electronic structure methods and their use in guiding alloy and ceramics development including: the KKR-CPA theory of the electronic structure and phase stability of alloys; the parallel SCPW cluster technique and its use in the study of intergranular films and the effects of rare earth additions in ceramics; the massively parallel LSMS method and spin dynamics calculations of the magnetic structure of alloys and nanostructures. First principles methods have been used to: develop a differential binding energy model to predict interfacial adsorption and its effect on ceramic grain growth; study the magnetic structure of FePt nanoparticles in the size range 2-5nm; and understand the role of vacancies in nanocluster formation in ODS alloys. A full potential LSMS method as been developed that is capable of simultaneous relaxation of atomic and magnetic structure. We have developed an understanding of the interaction between moving dislocations and radiation induced nanometer-sized defects using MD simulation and also developed novel global optimization strategies for nanoparticle structural optimization and studied the structure of model Lennard-Jones alloy nanparticles.

Program Impact: Our FLAPW calculations have supported alloy design of Ni-, Fe-, and Ti-based aluminides, and Mo-, Ti-based silicides, and have set the standard for first-principles calculations of ordered intermetallics. Our first-principles SCPW studies support forefront ceramics research here and abroad and have provided a basic understanding of microchemical effects of dopants on the mechanical properties of structural ceramics. Many KKR-CPA codes used around the world had their genesis in ORNL codes. A version of the constrained local moment method developed at ORNL is being taken up by research groups in Europe. We have played a leadership role in the overall development of the field of radiation materials science and materials applications in fission reactors, the SNS, and future fusion reactors. We are recognized leaders in applying parallel computing to materials science and the development and use of global optimization techniques for nanostructure optimization.

Interactions:
Internal–six divisions and ten experimental and theory groups
External–six national laboratories, eight US and seven foreign universities, three major corporations and four international research institutes. Past and current CRADAs include: IBM, Honeywell, Motorola, and Nonvolatile Electronics, Inc.

Recognitions, Honors, and Awards:
Selected: C. L. Fu: ISI 1000 Most Cited Physicists; 2002 TMS Champion H. Mathewson Medal; G. S. Painter: APS Fellow; G. M. Stocks: APS Fellow, Computerworld Smithsonian Laureate (2000), Gordon Bell Award (3); J. Barhen: NASA Space Act Awards (1995, 2002), R&D 100 Award (1998); V. Protopopescu: R&D 100 Award (1998, 2005); R. E. Stoller: Fellow, ASTM, ASM International, ANS Fusion Energy Division 2004 Outstanding Achievement Award.

Personnel Commitments for FY2007:
G. M. Stocks (80%), C.-L. Fu (70%), G. S. Painter (90%), R. E. Stoller (30%), Yu. Osetskiy, (40%), D. M. Nicholson (10%), J. Barhen (30%), V. Protopopescue (20%); N. Imam (30%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $2995K **FY06 BA** $2563K **FY07 BA** $2393K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 01 0

FWP: Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon

FWP Number: ERKCM43

Program Scope: Development of a broad science foundation to identify and understand the atomistic mechanisms of metal-assisted hydrogen storage in nanostructured carbons. The research is organized on three interactive levels: (1) First-principles computations for simulation of hydrogen interactions with graphite-like structures and prediction of optimal material structures and properties; (2) Based on the theoretical calculations, synthesis of appropriately modified metal-doped carbons, and (3) In-depth examination of the nanostructures of the carbon substrate and metal catalyst particles, and correlation of these structures with the hydrogen storage characteristics of the fibers.

Major Program Achievements:

- Using first-principle and Grand Canonical Monte Carlo simulations, calculated adsorption energy of H_2 between graphene layers as a function of interlayer spacing and determined theoretical limits of H_2 uptake versus pressure and temperature.
- Acquired a better understanding of the relationship between molecular composition and spinning conditions of pitch fractions obtained by dense gas extraction fractionation technique used for control of molecular weight in pitch.
- Improved control on synthesis and obtained Pd-doped activated carbon fibers (Pd-ACF) with 3-5 nm Pd particles and large volumes of narrow micropores in the pore size range (<0.7 nm) where theoretical predictions indicate maximum adsorption energy for H_2 confined between opposing carbon walls.
- Discovered isolated single Pd atoms present in Pd-ACF samples using aberration-corrected high-resolution scanning electron microscopy. This is an important finding, because single atoms of transition metals stabilized on graphene structures may exhibit the properties of Kubas-type complexes.
- Based on temperature effects on H_2 adsorption isotherms and in-situ high-pressure XRD data, obtained a better understanding of the role of Pd (and Pd hydride) particles in the mechanism of H_2 uptake at various temperatures.
- Obtained indirect evidence in support of the spillover mechanism at ~300 K from preliminary results on dynamics of molecular and atomic hydrogen on Pd-ACF from inelastic neutron spectroscopy studies.

Program Impact: This research will provide unique knowledge related to a sound understanding of the fundamental factors that influence hydrogen sorption on carbon materials and how they can be manipulated to attain desired storage capacities.

Interactions:
Internal–Electron Microscopy Group, Materials Science and Technology Division; Center for Nanophase Materials Sciences
External–Clemson University; NIST; University of Virginia; Penn State University; Active participation, IEA Hydrogen Implementing Agreement: Project No. N-2, "Effect of Metal Doping on the Hydrogen Storage Capacity of Activated Carbon Fibers" and Project No. N-1,"Metal-Carbon IEA Collaboration"

Recognitions, Honors and Awards:
Nidia Gallego: Secretary/treasurer of American Carbon Society; Cristian Contescu: Editorial Board, *Carbon*, 2007; Editor, 2nd Edition, *Dekker Encyclopedia of Nanoscience and Nanotechnology*; Jamie Morris: Co-organizer of two TMS symposia, 2007

Personnel Commitments for FY 2007:
N. C. Gallego (20%), C. I. Contescu (50%), J. R. Morris (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY05 BA $450K **FY06 BA $**567K **FY07 BA $**567K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 01 0

FWP: Scanning Transmission Electron Microscopy: Atomic Structure and Properties of Materials

FWP Number: ERKCS89 (ERKCS18 and ERKCS30)

Program Scope: The successful implementation of aberration-corrected scanning transmission electron microscopy in the last few years has more than doubled lateral resolution and provided major additional benefits, including nanometer-scale depth resolution, single atom sensitivity in both imaging and spectroscopy, and the ability to form simultaneous phase-contrast and *Z*-contrast images. These new capabilities are explored and applied to the outstanding materials issues not previously accessible in metals and alloys, structural ceramics, quasicrystals, complex oxides, superconductors and semiconductor device structures. Data from microscopy is combined with first-principles theory to provide insights into key issues in condensed matter and materials physics, chemical sciences and nanoscience. Increasing emphasis is being placed on quantitative comparison to theoretical image simulations for both *Z*-contrast microscopy and electron energy loss spectroscopy.

Major Program Achievements: Our aberration correction program has brought significant instrumental breakthroughs: the first direct imaging of a material with sub-Ångstrom resolution, spectroscopic identification of a single atom within a bulk material, and the demonstration of three-dimensional atomic-resolution imaging through depth-sectioning. These capabilities have enabled breakthroughs in many areas of materials, including grain boundary structure-property relationships in superconductors and ceramics, dislocation core structures in complex intermetallics, advanced semiconductor device structures, electronic phase separation and interfacial charge transfer in complex oxides.

Program Impact: Results have stimulated the widespread application of aberration-corrected scanning transmission electron microscopes, and major centers either include or plan to add such instruments in the near future. We have demonstrated over the last decade how coupling microscopy with first-principles theory offers quantitative insights into the atomic origins of materials properties, and this has become widely adopted. Papers have been accepted in the high impact journals *Science*, *Nature*, *Nature Materials*, *Physical Review Letters*, and the *Proceedings of the National Academy of Science*, as well as in more specialized journals. Numerous review articles have appeared in encyclopedias and books. Program is actively involved in scientific outreach with visits from researchers, university professors, teachers and students at all levels.

Interactions:
Internal—Materials Science and Technology Division: Materials Theory, Thin Film and Nanostructures, Correlated Electron Materials, Ceramic Science and Technology, Physical Chemistry of Materials and Alloying Behavior and Design Groups; Chemical Sciences Division: Surface Chemistry and Heterogeneous Catalysis Group.
External—Universities: Vanderbilt; Tennessee; North Carolina State; North Carolina A&T; South Carolina; Illinois, Chicago; Illinois, Urbana-Champaign; Northwestern; Brown; Minnesota; Drexel; Washington; Alabama; Tokyo, Japan; Paris, France; Oxford, UK; Melbourne, Australia; Madrid, Spain; Cadiz, Spain; Barcelona, Spain; Milan, Italy; Seoul National, Korea. National Institutes: LBL; BNL; ANL; NREL; INL; Polish Institute of Physics, Warsaw, Poland; Chinese Academy of Sciences, Beijing, China, Korean Institute for Standars and Science, Daejeon, Korea; Industries: Nion, Pixon, Fischione, Sematech, Alcoa.

Recognitions, Honors, and Awards:
29 invited presentations in FY 2007; S. J. Pennycook: Institute of Physics Thomas J. Young Medal and Award, 2001, Fellow of the American Association for the Advancement of Science, 2004.

Personnel Commitments for FY 2007:
S. J. Pennycook (50%); M. F. Chisholm (70%); M. Varela (100%); A. Lupini (40%), S. Pantelides, Vanderbilt Distinguished Scientist (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 $1958K **FY 06** $2178K **FY 07** $2038K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP: Multiscale Mechanical Properties and Alloy Design

FWP Number: ERKCM06

Program Scope: This program develops fundamental understanding of mechanical behavior across multiple length scales in complex multiphase alloys. Of special interest are new mechanical phenomena that cannot be explained by conventional theories including size effects on mechanical properties, particularly at small scales, magnetic effects on strength and ductility, and stress-induced superelasticity in the absence of obvious structural transformations. The observed relationships between mechanical properties and microstructural features (controlled, as needed, by innovative processing techniques and characterized by state-of-the-art microanalytical tools) are used to model deformation and fracture processes. This understanding leads to the formulation of broad scientific principles for the design of advanced metallic materials for use in a variety of next-generation energy production and conversion applications.

Major Program Achievements: Developed a new technique for the synthesis of single crystal micro-pillars which avoids the surface damage inflicted by focused ion beam (FIB) milling, which is typically how pillars are fabricated for small-scale mechanical tests. Demonstrated that the as-grown pillars behave like dislocation-free materials and yield at the theoretical stress ($\sim G/26$, where G is the shear modulus) independent of pillar size. This is the first time that theoretical strength has been achieved in micro-pillar compression tests and suggests that the lower strengths measured in other studies could be the result of FIB damage. As a first step towards understanding effects of this damage, the nanomechanical responses of electropolished and FIBed (100) surfaces of Mo-alloy single crystals were compared. On the electropolished surface, pop-ins were observed on all load-displacement curves corresponding to a transition from elastic to plastic deformation at the theoretical stress ($\sim G/8$). Similar pop-ins were not detected on the FIBed surfaces indicating that FIBing introduces damage that eliminates the need for dislocation nucleation during subsequent deformation. A second effect of FIB milling is that it increased the surface hardness. Together, these effects could be the source of some of the size effects reported in the literature on micro-pillar tests.

Program Impact: The recent results generated by this program on small-scale mechanical behavior have stimulated worldwide scientific interest since they provide a new way to study and understand confinement effects on dislocation behavior. Over the years more than 30 symposia/workshops on mechanical behavior and alloy design were organized by the PIs, three of whom, C. T. Liu, E. P. George, and J. A. Horton, were identified by ISI as the world's most-cited authors in materials science during the past 20 years. Scientific principles developed by the PIs have been utilized in DOE applied programs, including EERE, Fossil Materials, and Defense Projects. Tech transfer efforts growing out of the PI's research have resulted in >20 patents and >20 licenses to manufacture products for energy-related applications. This type of high-impact research continues with the recent work on multiscale mechanical properties (e.g., 6 *Phys*. *Rev*. *Lett*. papers and one *Science* paper in the past 4 years).

Interactions:
Internal—Theory, X-Ray Scattering, and Microscopy groups, Materials Science and Technology Division
External—Universities (including Pennsylvania, Tennessee, Virginia, Brown, Kyoto, Tohoku, Ruhr, and Beijing Science & Tech.), other national laboratories, and domestic and international materials institutes (IMR and NIMS, Japan; MPI, Germany).

Recognitions, Honors and Awards:
12 invited presentations in FY 2007; E. P. George: 2005 MRS Ribbon Award for Outstanding Paper, 2000 Humboldt Award; C. T. Liu: elected to the National Academy of Engineering, 2004; *Acta Materialia* Gold Medal, 2001; J. A. Horton: ASM Fellow 2002

Personnel Commitments for FY 2007:
E. P. George (20%), J. A. Horton (20%), J. R. Morris (50%), Z. P. Lu (50%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 BA $1275K **FY 06 BA** $1295K **FY 07 BA** $1250K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP: Microstructural Design of Advanced Ceramics

FWP Number: ERKCM07

Program Scope: Theory and experiment are combined to define (1) the critical length-scale structural characteristics that dictate the properties of ceramics and and (2) how these can be tailored during processing to enhance properties or lead to new properties. The fundamental design concepts incorporate different length-scale characteristics into theoretical and analytical models that are used to tailor the behavior (e.g., toughness, mechanical reliability, creep resistance) of ceramics. The results provide a quantitative picture of the mechanisms that enhance the mechanical behavior of monolithic ceramics, composites, multilayer systems and coatings.

Major Program Achievements: Developed fundamental understanding of the segregation of additive elements to, and adsorption at, grain surfaces in ceramics, which was confirmed by atomic-scale observations. While additives have been used to aid in the densification of ceramic powder compacts, additives can also control the structural features and, thus, the final properties of ceramics. This work has developed the fundamental theory combined with critical experimental observations that define how various additive elements control the evolution of microstructure through atomic level differences in their behavior. Only now has it been understood that each additive element can exhibit quite different adsorption at grain interfaces and why this occurs. Predicted differences in adsorption behavior of rare earth elements in silicon nitride ceramics have been experimentally confirmed, as has the differences in ordering of the adsorbing atoms at the grain interfaces as well as the relative site specific binding strengths. With MgO, microstructural evolution is dictated by the differences in adsorption behaviors of the rare earth additives. However, microstructural evolution during densification can be altered when RE_2O_3 additives are combined with SiO_2. This occurs as densification proceeds, in each case by the formation of a liquid phase, but the viscosity is substantially higher with SiO_2, which retards microstructure evolution mechanisms.

Program Impact: By understanding the mechanisms by which additives influence microstructural evolution, including those atomic-scale processes, it is now possible to use microstructural tailoring to overcome the brittleness issues associated with ceramics and devise radical changes in behavior (e.g., high thermal conductivity in silicon nitride). The predicted (and confirmed) differences in the degree of segregation and adsorption for various additive elements influence critical phenomena (e.g., phase transformations, grain growth) that dictate the evolution of microstructure during the densification of ceramics. Based on this approach, major advances in the development of fracture resistant ceramics have been achieved and provide new material concepts for advanced energy systems. These findings on silicon nitride, a compositionally and structurally complex ceramic, are now being recognized as having wide scale impact on ceramic materials.

Interactions:
Internal–Materials Science and Technology Division: Materials Theory, Alloy Behavior and Design, and Electron Microscopy Groups.
External–University of Tokyo, Oxford University, University of Tennessee, University of Karlsruhe, Commissariat à l´Énergie Atomique-Saclay, Korean Institute of Machinery and Materials.

Recognitions, Honors and Awards:
P. F. Becher: member editorial committee of *Materials Review*, ASM International; Academician of World Academy of Ceramics; Fellow, American Ceramic Society; member of National Materials Advisory Board (National Academies); Highly Cited Materials Science Researcher, ISI Web of Knowledge; American Ceramic Society: 2006 Edward Orton Lecturer, Past President, Associate Editor, *J. Amer. Ceram. Soc.*
C. H. Hsueh: World Innovation Foundation and American Ceramic Society Fellow; Highly Cited Materials Science Researcher, ISI Web of Knowledge; Associate Editor, *J. Amer. Ceram. Soc.*

Personnel Commitments for FY2007:
P. F. Becher (90%), C.-H. Hsueh (40%); M. J. Lance (10%)

Authorized Budget (BA):
FY05 BA $1001K **FY06 BA** $981K **FY07 BA** $981

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP: Self-Assembly of Stable Nanoclusters in Metallic Matrices

FWP Number: ERKCM42

Program Scope: This work seeks an understanding of the formation mechanism, thermal stability, and hardening behavior of extremely stable nanoclusters in metallic alloys fabricated by mechanical alloying (MA) and innovative processing. Initial work focuses on ferritic alloys, with the intention to extend our studies to include other metallic systems containing stable nanoclusters. This research involves theoretical and experimental studies of the formation mechanism and thermal stability of stable nanoclusters in metallic systems and investigation and modeling of the unusual hardening behavior at ambient and elevated temperatures.

Major Program Achievements: Atomic-scale characterization established that these nanoparticles have extraordinary thermal stability. Scanning transmission electron microscopy (STEM) showed the Fe matrix contains clusters with diameters ranging from 2 to 5 nm and an average spacing of ~12 nm. Atom probe results and In-situ small angle neutron scattering revealed bi-model particle size distribution with local maxima around 2 and 12 nm, respectively. The 2-nm nanoclusters demonstrated extraordinary thermal resistance at temperatures to 1400°C. First-principles calculations indicated that stable bonding between oxygen and vacancies is necessary and that O-vacancy binding energies are several times greater than that of corresponding C- and N-vacancy structures. First-principles results also predicted that vacancies play an indispensable role in enhancing the oxygen/cluster binding energy in the presence of Ti and in inducing the attractive Y-O interaction in Fe. The strong oxygen-vacancy binding makes stabilization of coherent nanoclusters in the Fe lattice feasible. The importance of magnetism for the unusually high O-vacancy binding energy (-1.45 eV) was discovered by calculating the O-vacancy binding energy in a hypothetical non-magnetic Fe matrix: with atomic positions fixed at the corresponding spin-polarized case, non-spin-polarized calculations reveal that the binding of O with its nearest neighbor Fe-vacancy was much weaker (-0.35 eV). Transmission electron microscopy (TEM) indicated that these clusters can be effective barriers to dislocation movement, even at 1100°C In the anomalously large (10-30 μm) grains grown by prolonged annealing of nanocluster alloys at 1000°C, TEM observations clearly showed the interaction between the nanoclusters and the dislocations, suggesting that the nanoclusters are responsible for the high creep strength.

Program Impact: The existence of nanoclusters that are thermodynamically stable at elevated temperatures is a truly intriguing issue in the materials community because of both the scientific implications of such a phenomenon and the potential applications. By successfully combining theoretical calculations and experimental studies, this project is providing new understanding regarding nanoclusters that are kinetically or thermodynamically stable at high temperatures. The scientific principles are expected to have broad applicability in the synthesis of next-generation nanostructured materials with high temperature capability for engineering applications.

Interactions:
Internal–DMSE efforts at ORNL in theory (ERKCM01), electron microscopy (ERKCS89), atom probe (ERKCM03), and alloy design and mechanical properties (ERKCM06); SNS
External–Berlin Neutron Scattering Center, Hahn-Meitner-Institute, Berlin; ANL; Ohio State University; Universities of Tennessee, Bochum (Germany), and Central South University (China)

Recognitions, Honors, Awards:
C. T. Liu: Member of National Academy of Engineering, 2004, and Foreign Member, Chinese Academy of Engineering, 2005; M. K. Miller: 2004 MSA Cosslett Award; Co-Chair, Focused Interest Group on Atom Probe, MSA

Personnel Commitments for FY 2007:
C. T. Liu (25%), M. K. Miller (10%), J. A. Schneibel (10%), M. F. Chisholm (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 BA $374K **FY 06 BA** $317K **FY 07 BA** $367K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 03 0

FWP: Atomistic Study of Bulk Metallic Glasses

FWP Number: ERKCM40

Program Scope: The purpose of this project is to develop novel theoretical and experimental approaches to study the atomic level phenomena in metallic glasses. In particular, we study glass transition, atomic transport, glass formation and mechanical deformation of metallic glasses through such approaches and aim at achieving an understanding of the mechanisms of glass formation and deformation at an atomistic level. While the recent development of bulk metallic glasses has drastically improved the prospect of application of metallic glasses as a structural material, the science of metallic glasses, in particular at the atomistic level, is only in its infancy. Our goal is to establish general principles that could guide the effort for further alloy development and improvement.

Major Program Achievements: A major question we address is why the viscosity of a liquid metal changes so enormously between the glass transition temperature and the melting temperature of a crystal, with little underlying changes in the atomic structure. Using molecular dynamics simulation and proper choice of functions to characterize the structure and dynamics, such as bond fluctuations and stress correlation functions, we have shown that the structure and dynamics of a liquid metal change at a well-defined crossover temperature, well above the glass transition temperature. Below the crossover temperature local dynamic networks of atoms are formed, leading to the glass transition. These results give a much clearer picture of the process with which the randomly moving atoms in a high temperature liquid become more correlated as the liquid is cooled, and finally condense into a glass. We have developed the topological fluctuation theory which impressively succeeds in qualitatively calculating the glass transition temperature. This theory is being extended to elucidate these findings..

Program Impact: Our theory of topological fluctuations in liquids and glasses will impact field of glasses at large, not only metallic glasses but covalent and molecular glasses as well. While the theories of crystalline solids have been highly developed, the physics of liquids and glasses lag well behind. Our theory will advance this important but less developed field significantly, potentially impacting a wide range of fields from engineering, physics, chemistry, medicine and biology.

Interactions:
Internal–Center for Computational Sciences; Computer Science and Mathematics Division; Alloy Behavior and Design Group; X-Ray Research and Applications Group; High Temperature Materials Laboratory, Materials Science and Technology Division; HFIR; SNS
External–Los Alamos National Laboratory; Ames Laboratory; Chinese Academy of Sciences; California Institute of Technology; University of Virginia.

Recognitions, Honors and Awards:
11 invited presentations in FY 2007, including several keynote lectures; T. Egami: Senior Researcher Prize, International Symposium on Metastable and Nano Materials (ISMANAM), 2006; Bertram Eugene Warren Diffraction Physics Award, American Crystallographic Association, 2003; John Wheatley Scholar, Los Alamos National Laboratory, 2002; contract to write a book on "Physics of Liquids and Glasses" by Cambridge University Press.

Personnel Commitments for FY2007:
T. Egami, ORNL/UT Distinguished Scientist (50%), J. R. Morris (10%), Y. Y. Braiman (90%), D. M. Nicholson (10%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $955 **FY06 BA** $740K **FY07 BA** $740K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 05 0

FWP and/or subtask Title under FWP: Design and Synthesis of Nanomaterials

FWP Number: ERKCM38

Program Scope: This research is focused on the understanding of mechanisms that control the synthesis of nanostructured material systems. Specifically, our primary focus is on catalytic synthesis of carbon nanostructures and the synthesis of nanoparticles encapsulated within these carbon nanostructures. The process of formation and evolution of these carbon-catalyst systems involve dynamical reciprocal influences of both components resulting in the intertwined controlled co-synthesis of two nanostructured materials with complementary functions. We investigate the role of the catalyst material composition, crystallographic orientation, and shape on the atomic structure of the resulting carbon nanofibers, study the link between the macroscopic parameters of plasma enhanced chemical vapor deposition reactor environments and the atomic scale processes at the catalyst nanoparticles, and elucidate the influence of the curved graphitic structure on the evolution of the shape and structure of the catalyst nanoparticle. A second connected theme of this research is to gain insight on the magnetic properties of catalytic nanoparticles and the formation of ordered alloys during and after co-synthesis and after post-synthesis annealing.

Major Program Achievements: A role of non-catalytic alloy components in controlled synthesis of carbon nanostructures in PECVD processes was studied based on Ni-Cu alloys. It was found that catalyst composition provided control over the resulting nanostructure shape, structure, and composition. Ultrasharp single-crystal Si nanocones resulted from the use of 100% Cu catalyst material in the C_2H_2-NH_3 dc plasma process. Controlled co-synthesis of FeCo alloy nanoparticles inside carbon nanofibers was established for a range of compositions; magnetic properties of the resulting nanopartilces has been characterized. The dewetting process of nanoparticle formation from a thin film has been studied in detail, and was shown to be governed by several parameters rather than only film thickness. $FeNi_3$ alloy nanoparticles were synthesized to study the influence of nanoscale confinement on order-disorder phase transition in alloy nanoparticles, but no ordered $FeNi_3$ alloy state has been found so far. However, significant segregation of Fe from the nanoparticle was observed with molecular dynamics simulations showing that Fe moves toward outer layers. The relationship of catalyst shape, catalyst orientation, growth conditions with growth rate and graphitic carbon structure has been elucidated. We found strong dependence of growth rate and angle of graphene sheets with respect to nanofiber axis. The configuration of a graphitic overlayer on a clean Ni(111) surface have been investigated using density functional theory (DFT). A new stable bridge-type structure has been found with implications for the model of nanofiber synthesis. A phenomenological model of the interaction between catalyst and graphitic structure has developed, which indicates an intrinsic instability in the solution for a curved graphite-particle interface near nanofiber center.

Program Impact: The fundamental understanding of this co-synthesis process make possible the precise control of synthesis and assembly of magnetic nanoparticles, carbon nanostructures, and their bi-functional combination. The work on controlled synthesis and directed assembly is already having an impact in areas such as electrodes for batteries and super capacitors, magnetic storage media, interface to and delivery of materials (e.g. genes, proteins, and therapeutic agents) to living cells, biomimetic structures, and field emission devices.

Interactions:
Internal–Multiscale Mechanical Properties and Alloy Design (ERKCM06); Theory of Complex Materials (ERKCS91); Theoretical Studies of Formation, Stability, and Properties of Low-Dimensional Materials (ERKCS92)
External–Florida Atlantic University; University of Tennessee; LANL; University of Wisconsin; Columbia University

Recognitions, Honors and Awards:
3 invited presenations in FY 2007; M. L. Simpson: Elected Fellow of IEEE

Personnel Commitments for FY2007:
M. L. Simpson (20%), A. V. Melechko (70%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $483K **FY06 BA** $448K **FY07 BA** $473K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 01 0

FWP: X-Ray Scattering and Microscopy

FWP Number: ERKCS73

Program Scope: This program performs fundamental investigations of materials microstructure and evolution on mesoscopic length scales and atomic scale investigations of local chemical ordering and the dynamical electronic structure of materials. High-brilliance synchrotron x-ray beams at the Advanced Photon Source (APS) are exploited in connection with innovative instrumentation, advanced measurement techniques, and theory collaborations. Advanced x-ray focusing optics and three-dimensional (3D) submicron-resolution x-ray microscopy techniques are pursued. Novel neutron optics and new scattering techniques are developed to extend neutron diffraction investigations to 3D measurements of materials structure and sample sizes on length scales of tens of microns. Long-standing issues associated with 3D grain-growth, deformation, and strain localization are addressed using microbeams. Non-resonant inelastic x-ray scattering is used for studying the dynamical electronic structure of strongly correlated electron materials, elastic diffuse scattering for probing short-range atomic structure in alloys, and Bragg scattering for determining strain and phase in bulk materials and the structure and epitaxy of thin-films.

Major Program Achievements: Developed 3D x-ray structural microscopy for submicron-resolution investigations of crystal microstructure and strain tensor distributions on XOR/UNI (Sector 34) at the APS; developed new large-q, non-resonant inelastic x-ray scattering technique to study *d-d* excitations in strongly correlated materials in collaboration with theory; demonstrated sub-100 nm polychromatic x-ray focusing optics, and polychromatic neutron optics with less than 100 μm diameters; performed the first micron-resolution, nondestructive, 3D measurements of the Nye dislocation density tensor over mesoscopic length scales in a deformed material and the first 3D thermal grain-growth measurements in a polycrystalline material; performed the first absolute, nondestructive measurement of plastic deformation with submicron resolution over mesoscopic length scales using microindents; pioneered new methods to study fundamental properties of solid solution alloys.

Program Impact: The development of 3D x-ray structural microscopy (3DXSM) provides direct, quantitative links between mesoscale microstructural measurements and first-principles-based theory and modeling that are needed to develop a predictive understanding of materials behavior; our implementation of 3DXSM on 34-ID-E is the only x-ray facility with 3D crystal structure, orientation, and local elastic and plastic strain tensors characterization at submicron resolution. The x-ray optics and polychromatic microbeam analyses developed are being integrated into synchrotron microbeam facilities worldwide. The ability of non-resonant inelastic x-ray scattering to study dipole-forbidden excitations opens a new window to study strongly correlated materials. Polychromatic neutron focusing optics increase neutron fluxes by two orders of magnitude for sub-100 micron beams, which will facilitate neutron scattering measurements for high pressures cells and small sample volumes.

Interactions:
Internal–Epitaxial oxide films (ERKCS80), mechanical behavior (ERKCM06), condensed matter theory (ERKCS08); SNS; HFIR
External–NIST; APS, ALS, ESRF, Canadian, Australian, and Pohang (Korea) Synchrotron facilities; LANSCE, IPNS, ILL and Chalk River; BNL, NSLSII; MPI-Düsseldorf; fourteen universities; Institute Metal Physics, Ukraine; Alcoa Technical Center; Northrup-Grumman; Ford Motor Company; General Motors; IBM; NASA

Recognitions, Honors, and Awards:
More than 30 invited presentations in FY 2005-2007; G. Ice: 2005 Maslen Fellow, ASM Fellow, Co-editor, *J. Synchrotron Radiation*, APS User's Organization Steering Committee (2006-2007), NSLS-II Experimental Facilities Committee (2006); B. C. Larson: Guest Editor, *MRS Bulletin* (March 2004), CHESS Policy and Advisory Board; J. Z. Tischler: Chair, APS Beam Time Allocation Committee (2002–2007); 3 American Physical Society Fellows (Larson, Ice, and Budai); ORNL Scientific Research by Team Award, 2002 (Ice and Larson)

Personnel Commitments for FY 2007:
B. C. Larson (70%); G. E. Ice (80%); J. D. Budai (100%); J. Z. Tischler (70%); J. Pang (100%); E. Specht (30%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 $2450K **FY 06** $2375K **FY 07** $2375K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Epitaxial Complex Oxides: Growth Mechanisms and Cooperative Phenomena

FWP Number: ERKCS80

Program Scope: This project addresses the fundamental question of how to understand and control cooperative phenomena that emerge at the nanoscale and, in particular, how to tune and enhance such properties through artificial nanoscale coupling. To achieve this goal, emphasis is first placed on understanding the growth mechanisms that lead to the formation of atomically sharp interfaces in the epitaxial growth of complex layered materials, using highly specialized tools such as time-resolved surface x-ray diffraction. Second, this work focuses on understanding the properties of the constituents of epitaxial assemblies, i.e. ultrathin epitaxial layers and wires, by studying how their magnetic, ferroelectric and transport properties are affected by spatial constraints, proximity to dissimilar phases, and interfaces (including electronic effects, strain, and chemical segregation). Finally, complex structures, including two- and three-component superlattices, as well as fractional superlattices (epitaxial structures containing embedded islands or wires formed using self-assembly or lithographical patterning) are designed and analyzed. Theoretical insights into synthesis and properties aid in the design of these materials. A special emphasis is placed on combining strongly dissimilar properties (such as ferroelectricity and ferromagnetism) in one monolithic structure, with the goal of creating entirely new functionalities and coupled properties as well as of understanding the underlying physics.

Major Program Achievements: Used surface x-ray scattering to unambiguously demonstrate that homoepitaxial growth in pulsed-laser deposition occurs via a two-layer (or three-level) growth front rather than in a simple layer-by-layer fashion. Initiated diffuse surface x-ray scattering experiments to study the evolution of island sizes at the growth front in perovskite film deposition. Demonstrated that PLD can yield epitaxial heterostructures with interface quality previously thought to be possible only in molecular-beam epitaxy. Experimentally verified strain insensitivity of the ferroelectric polarization in $BiFeO_3$ and $Pb(Zr,Ti)O_3$ films. Investigated ferroelectric properties in superlattices containing $BaTiO_3$, $SrTiO_3$, and $CaTiO_3$. Used strain and inter-layer coupling to obtain ferroelectric and antiferroelectric order in superlattices of otherwise non-polar perovskites. Observed antiferroelectricity in $BiCrO_3$ multiferroic films and ferroelectricity in $BiCr_xFe_{1-x}O_3$ alloys. Collaborated with SUNY-Buffalo to investigate the anomalous Hall effect in films of $Ca_xSr_{1-x}RuO_3$. Developed and applied the ORNL temperature-gradient and compositional-spread growth methods to the discovery of high-k dielectric perovskites with practical crystallization temperatures, the development of catalysts for carbon nanotube growth, and the investigation of optoelectric materials.

Program Impact: Leading international effort in the design and synthesis of artificial oxide heterostructures with enhanced properties and in using time-resolved in situ diagnostics to understand pulsed laser deposition processes for thin film growth. Results having great impact in definitively exploring transition metal oxide cooperative phenomena and in developing testing of theoretical models.

Interactions:
Internal—Oxide heterostructures synthesized with atomic-layer control are indispensable to test theory/modeling using leadership scientific computing facilities and to exploit atomic-scale spectroscopy based on *Z*-contrast scanning transmission electron microscopy.
External—U. Wisconsin-Madison; Rutgers; ANL; Penn St.; U. of Arkansas; MPI-Stuttgart; Seoul National; Cornell; U. Potsdam; U. Florida; U. Mass.; SUNY Buffalo; U. Tenn.; George Washington; Embry Riddle; Harvard; Dresden; UC Davis. Interactions include the exchange of samples, visits to use characterization and measurement equipment at collaborators' institutions, and joint experimental/theoretical work.

Recognitions, Honors, and Awards:
6 invited presentations in FY 2007; H. M. Christen: Co-organizer of a Division of Materials Physics focus Topic Session at 2007 APS March meeting

Personnel Commitments for FY 2007:
H. M. Christen (30%), G. Eres (40%), B. C. Larson (20%), J. Z. Tischler (30%), C. M. Rouleau (25%), H. N. Lee (40%), J. Shen (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 BA $1231K **FY 06 BA $**1231K **FY 07 BA $**1201K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Growth Mechanisms and Controlled Synthesis of Nanomaterials

FWP Number: ERKCS81

Program Scope: This project explores the link between growth mechanisms and resulting nanoscale structure in order to discover and controllably synthesize novel nanomaterials with enhanced properties. Materials synthesis in this project relies heavily on non-equilibrium growth techniques that are coupled with in situ time-resolved diagnostics to simultaneously probe the processing environment and the kinetics of nanomaterial nucleation and growth. Through these measurements, predictive theory, and the development of associated growth models, an understanding is developed for how the structure, composition, and defects in nanomaterials are determined during synthesis. Both high- and low-temperature synthesis methods are explored to understand the differences in physical and chemical properties of nanomaterials formed under vastly different kinetic regimes. The focus is on quasi-0D and -1D structures (nanoparticles, nanowires, nanotubes). The program concentrates on intriguing fundamental questions common to different classes of materials which form nanostructures by both spontaneous self-assembly or through the assistance of metal (or metal-oxide) catalyst nanoparticles using the examples of Si- and C-quantum dots, nanotubes of C and BN, C-nanohorns, and nanowires of Si, $Ca_xMo_yO_{7-y}$, SnO_2, Cu-TCNQ, Ag-TCNQ, and ZnO.

Major Program Achievements: (1) Developed coordinated imaging and interferometry techniques with pulsed laser heating and gas delivery to directly measure the growth kinetics of carbon nanotube arrays, enabling the formation of a quantitative model of nanotube growth. (2) Developed the basic understanding, heat transfer models, and in situ diagnostics of high power laser vaporization synthesis of single wall carbon nanotubes and nanohorns. (3) Developed the scientific understanding of factors governing catalyst efficiency in nanotube growth by chemical vapor deposition. (4) Discovery of an initial stage in vertically-aligned nanotube array growth with highly non-linear kinetics indicating polymerization reactions in carbon network formation. (5) Correlation of defect formation in nanotube growth with the molecular structure of the hydrocarbon source gas, as indicated by low-temperature transport measurements on individual nanostructures.

Program Impact: Pioneering work in the investigations of nanostructure synthesis utilizing time-resolved in situ diagnostics of nonequilibrium growth environments, such as pulsed laser vaporization and chemical vapor deposition processes for single-wall carbon nanotube growth. Development of accurate growth models and of unique nano-structured materials, many of which have potential for energy applications.

Interactions:
Internal—Well-characterized and purified single-wall carbon nanotubes and nanotube arrays form the basis for numerous interactions at ORNL involving fundamental chemistry, effects of strength and thermal transport in polymer nanocomposites, electronic enhancements in organic electronics and sensors, and functionalization (Materials Science and Technology and Chemical Sciences Divisions; Center for Nanophase Materials Sciences).
External—Collaboration/subcontract on continued growth processes for aligned nanostructures with James Tour (Rice). Twenty other collaborations with universities. Collaborations on carbon-based materials with Argonne, Brookhaven, and Sandia National Laboratories. Collaborations with 12 other U.S. and foreign national/industrial research labs.

Recognitions, Honors, and Awards:
8 invited presentations in FY 2007; D. B. Geohegan: Co-organizer of international conferences (including the 9th International Conference on Laser Ablation, Spring MRS Symposium on Carbon Nanotubes and Related Nanostructures, and Synthesis and Photonics of Nanoscale Materials, SPIE 2007); C. M. Rouleau: Key Contributor Award Recipient, ORNL .

Personnel Commitments for FY 2007:
D. B. Geohegan (30%); A. A. Puretzky (30%); G. Eres (40%); C. M. Rouleau (25%); I. Ivanov (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 $944K **FY 06** $944K **FY 07** $924K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Correlated and Complex Materials

FWP Number: ERKCS82

Program Scope: Focus is on discovery and investigation of novel cooperative phenomena and new forms of order in complex transition metal oxides and Zintl phase intermetallic compounds. The primary tools used by the program are synthesis, compositional tuning, and crystal growth of new materials, as well as X-ray and neutron diffraction, electrical and thermal transport, heat capacity, and magnetization. Phenomena of interest include charge and orbital ordering, coupling of magnetism and dielectric behavior, spin-state transitions, effects of inversion symmetry breaking on superconductivity, vortex pinning and dynamics, low carrier density ferromagnetism, anomalous Hall effect and other Berry phase effects, and the origin of relaxor behavior in ferroelectric materials. A large fraction of the effort is devoted to the discovery of new materials and the growth of large single crystals of fundamental interest to condensed matter physics.

Major Program Achievements: Grown single crystals of Fe_2OBO_3 for the first time and discovered nearly perfect ionic charge order as well as an unexpected incommensurate phase; synthesized high quality crystals of $LuFe_2O_4$, in which charge order produces ferroelectricity and solved the magnetic structure using neutron scattering; Grown crystals of Na_xCoO_2, $Ba_{1-x}Sr_xCoO_4$, and $Ca_3Co_4O_9$, and studied their physical properties**;** Observed dopant-induced nanoscale inhomogeneities in crystals of $Ca_{2-x}Sr_xRuO_4$ and studied a purely electronic Mott transition at the surface; studied Luttinger liquid formation in "purple bronze" $Li_{0.9}Mo_6O_{17}$; Studied the 200 K structural phase transition in $Cd_2Re_2O_7$, and learned that this transition is "ferroelectric" in that it breaks inversion symmetry; Observed slow tunneling of Eu ions in the clathrate $Eu_8Ga_{16}Ge_{30}$; Anomalous Hall effect (AHE) studies in low carrier density (Zintl) ferromagnets: Several key predictions from theory have been verified. In the underscreened Kondo ferromagnet $Yb_{14}MnSb_{11}$, discovered the first example of a sign change in the AHE with crystallographic orientation**;** Interdisciplinary work on synthesis, properties measurements, and interpretation has demonstrated interplay between tuning of the quantum growth stability and robust superconducting vortex confinement in ultrathin pure metals and alloys. Research on cuprate superconductors has shown consistency of observed loss-free currents with model theories of vortex pinning by material nanostructures; Discovered new effects in the ferroelectric-to-relaxor cross-over transition as a function of the tantalum-to-niobium ration in the mixed solid solution KTN system and three new dielectric relaxation processes due to polarization effects in Ca-doped potassium lithium tantalate crystals.

Program Impact: Achievements described above are primarily scientific discoveries, and their main impact is on the direction of science. Several of the materials studied are promising candidates for advanced thermoelectric materials. This program is also helping to elucidate the fundamental, complex interaction among vortices and material nanostructures that lead to the vortex immobilization required to support energy loss-free electric currents. These achievements have led to many high-impact publications and invited talks, and are receiving >500 citations/year.

Interactions:
Internal–Materials Science and Neutron Scattering Sciences Divisions
External–Sixteen universities, ANL, BNL, LANL, SNL, Ames Laboratory, EPFL Lausanne (Switzerland), Jülich (Germany)

Recognitions, Honors, and Awards: 27 invited presentations in FY 2007. D. Mandrus: Fellow, American Physical Society (APS); B. C. Sales: Fellow, APS; Member Editorial Board, *J. Phys. Chem. Solids*, ORNL Distinguished Scientist Award, 2007; R. Jin: Women of Color Magazine and IBM Corporation "Rising Star of Technology" award, 2006; M. A. McGuire: Wigner Fellow; D. K. Christen: "Nano-50 Award" by *Nanotech Briefs*, Nov 2006"; J. R. Thompson: Associate Editor, *Appl. Sci. Lett.*, "Nano-50 Award" by Nanotech Briefs, Nov 2006**;** L. A. Boatner: Chair of the Division of Materials Physics of the APS; Fellow of the Mineralogical Society of America

Personnel Commitments for FY 2007:
D. G. Mandrus (90%), D. K. Christen (20%), J. R. Thompson (20%), B. C. Sales (90%), G. E. Jellison Jr. (20%), R. Jin (50%); E. W. Plummer, ORNL/UT Distinguished Scientist (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 BA $2104K **FY 06 BA** $2202K **FY 07 BA** $2090K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Emergent Behavior in Low-Dimensional Systems

FWP Number: ERKCS83

Program Scope: This work focuses on exploring physical properties of materials in reduced dimensionality, often at nanoscale dimensions, where changes in physical properties are anticipated due to confinement effects either quantum in nature or resulting from surface or interface effects. Attention is focused on magnetism, ferroism, charge order, spin order, and electron transport with particular emphasis on spin transport. Thus, materials receiving the greatest attention are those with novel magnetic, electronic, and interrelated ferroic properties. These materials include strongly correlated electronic systems such as transition-metal oxides where the complexity arises from nonlinear correlations between spin, charge, and lattice structure, novel combinations of conventional magnetic materials, and dilute magnetic semiconductors. Anticipated accomplishments are the discovery of novel physical properties and mechanisms that emerge from low-dimensional confinement.

Major Program Achievements: Discovered a purely electronic Mott metal-to-insulator transition at the surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ resulting from the broken translational symmetry which causes a compressional stress; Discovered and demonstrated the ability to tune the quantum stability and superconductivity of ultrathin metal alloys; Observed giant discrete steps in metal-insulator transition in perovskite Manganite wires; Discovery of Luttinger-liquid physics in quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ by scanning tunneling microscopy and photoemission; Observation of dopant-induced nanoscale electronic imhomogeneities in $Ca_{2-x}Sr_xRuO_4$ and $(La_{1-y}Pr_y)_{5/8}Ca_{3/8}MnO_3$; Direct evidence of Eu atom tunneling at 450 MHz in crystalline $Eu_8Ga_{16}Ge_{30}$; Characterized inversion breaking structural phase transition and report of a Goldstone-mode phonon dynamics in $Cd_2Re_2O_7$ using second harmonic generation; Synthesized FeGe nanowires on Ge that are strong ferromagnets below 200 K; Realized robust superconductivity in ultrathin, quantum-confined films of Pb, with strongly contrasting interactions of vortices with differing quantum structural defects; STM observation of a low-temperature disordered phase of α-Pb/Ge(111); Detailed STM study of the intertwined electronic and structural phase transitions and nanoscale inhomogeneities and fluctuations in the In/Si(111) interface; Optical study of interactions in a d-electron Kondo lattice with ferromagnetism; Investigated frozen low-spin interface in ultrathin Fe films on Cu(111); Observation of multiple Bosonic mode coupling in electron self-energy of $(La_{2-x}Sr_x)CuO_4$; Observation of the Fermi surface evolution and Luttinger theorem in Na_xCoO_2.

Program Impact: This program had generated several seminal works in discovery of emerging phenomena in materials with reduced dimensionality.

Interactions: Extensive internal collaborations exist within the Materials Science and Technology Division and with the Chemical Sciences Division and Center for Nanophase Materials Sciences. There are ~60 national and international collaborations leading to published papers and joint external proposals.

Recognitions, Honors, and Awards:
J. Shen: Guangbiao Chair Professor at Zhejiang University, Hangzhau, China; E. W. Plummer: Distinguished Alumnus Award, Lewis and Clark College; National Academy of Science; H. Weitering, Joint Institute for Advanced Materials chair of excellence

Personnel Commitments for FY 2007:
J. F. Wendelken (20%), J. Shen (10%), S. Kalinin (20%), E. W. Plummer, ORNL/UT Disniguished Scientist (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 $902K **FY 06** $944K **FY 07** $938K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 03 0

FWP: Integrated Multiscale Modeling of Molecular Computing Devices

FWP Number: ERKCM41

Program Scope: Self-assembled molecular electronics (ME) systems composed of many single-molecule devices are conceived as the most promising path to future computers with ultra-dense, ultra-fast, molecular-sized components, and as the likely candidate to continue Moore's law beyond silicon technology. However, there exist formidable barriers to their practical implementation. Experiments in ME are both difficult and very expensive. We are developing a comprehensive theoretical and computational framework, especially for the prediction of electron transport in single molecules in their real environment (i.e., in a single-molecule experiment or at a system level in a working device). Significant theoretical and mathematical issues must be resolved to make such modeling capability a reality. In order to address this goal, this proposal brings together a team of experts to address process, device and circuit modeling of molecular electronics and the underlying mathematics in a comprehensive and integrated fashion across time and length scales.

Major Program Achievements: With the materials funding stream of this multi-disciplinary and multi-institution project, ORNL has been focusing upon theory and code for quantum electron transport in molecular and nanoscale systems. Up to this point, we have developed a parallel code for computing quantum transport and made numerous applications to molecular and nanoscale systems including simulation of various atomic microscopies. Our most recent accomplishments include the following.

We have collaborated with the Vanderbilt groups to apply ab initio methods to improve force-field models of the chemical interaction of molecules with the gold surface used to model the Reed experiment. A cluster model has also been developed for comparison with periodic models since the accurate many-body methods can only work on finite systems.

Control of gating in carbon nanotubes via organic doping and mechanical/vibrational deformation has been examined with the very positive conclusion that such control is possible. This presents a possible path to the construction of computing/memory devices. This work has been published in peer reviewed journals.

Our development of a massively parallel transport code has continued, and we have made progress in demonstrating a solution to the inconsistency of the finite/open Hamiltonians used in the principal layer approach. A rigorous comparison of finite and periodic calculations with identical Gaussian bases and all-electron potentials is now underway.

Program Impact: Our new theoretical and computational tools are enabling more rigorous, complete and realistic modeling of molecular electronic devices and are already beginning to answer both fundamental and experimental questions. These codes will be widely available, including distribution as part of NWChem.

Interactions:
Internal–Center for Nanophase Materials Sciences
External–Center for Nanoscale Materials (ANL); North Carolina State University; Technical University of Toyohashi; Brown University.

Recognitions, Honors and Awards:
None

Personnel Commitments for FY2007:
V. Meunier (10%), X. G. Zhang (20%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY05 BA $180K **FY06 BA** $180K **FY07 BA** $185K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 03 0

FWP: Theory of Condensed Matter

FWP Number: ERKCS08

Program Scope: Research condensed matter physics theory using a broad range of computational and analytic approaches. The work includes the development and extension of modern theories of condensed matter and computational methods as well as applications. Present work includes highly correlated materials, superconductivity; ferroelectrics, materials design, magnetism and magnetic materials, magneto-transport, neutron scattering, multi-scale modeling, magnetic nanostructures, molecular electronics, and various aspects of grain boundaries, surfaces, and interfaces. The long term goals are (1) to support and guide experimental research at ORNL and elsewhere, especially neutron science, nanoscience and novel materials discovery and (2) to develop theoretical and computational approaches for designing novel functional materials and nanostructures.

Major Program Achievements: Prediction of a new oxide that is both ferromagnetic and polar using first principles calculations. Elucidation of the bonding in $(ReH_9)^{2-}$ based salts and prediction of the existence of new $(MnH_9)^{2-}$ salts. Discovery of a new spin glass phase in the double exchange model for colossal magnetoresistive manganites and other materials. Use of polynomial expansion methods and numerical simulations to show the fragility of the ordered phases of manganites. Establishment of the role of disorder in modifying photoemission spectra and Fermi surface measurements for Na_xCoO_2. Investigation of quantum size effects in Pb films from first principles including the role of the substrate. Performance of detailed simulations to investigate the adsorption of molecules on nanofacets and the resulting bonding patterns. Establishment of the electronic structure, and the features in it underlying magntodielectric response, in $Ni_3V_2O_8$, $K_2V_3O_8$ and other oxide magnetodielectrics. Explanation of low energy charge excitations in MgB_2 in terms of the interplay of collective and single particle modes.

Program Impact: The theoretical work supported by this FWP, in conjunction with experimental work at ORNL and elsewhere, has resulted in understanding of some of the most challenging and interesting condensed matter systems including various polar materials, unconventional superconductors, various correlated oxides, nanostructures and metal hydrides. This is recognized by numerous invited talks given at international meetings and at universities, and publications in high profile journals.

Interactions:
Internal–Center for Computational Sciences, Computer Science and Mathematics Division, X-Ray Scattering groups, Electron Microscopy Group, Low-Dimensional Physics Group, Superconductivity Group, Correlated Electron Materials Group, Materials Science and Technology Division; Neutron Scattering Sciences Division, Center for Nanophase Materials Science
External–U.S. Universities: Cincinnati, Clemson, Georgetown, Harvard, Oklahoma State, Stanford, Texas A&M, Vanderbilt, William and Mary, California (Davis, Irvine, Los Angeles, Santa Barbara, San Diego), Florida, Minnesota, Tennessee, Texas (Austin and Arlington) and Wisconsin.; Other Laboratories: Geophysical Laboratory, Naval Research Laboratory; Foreign: top institutions in Argentina, Austria, China, Denmark, France, Germany, India, Italy, Japan, and Sweden.

Recognitions, Honors, and Awards:
24 invited presentations in FY 2007; A. Moreo: Member of nominating committee for Division of Computational Physics of the APS; S. Pantelides: AAAS Fellow; E. Dagotto: Distinguished Scientist; 5 APS fellows; members of several editorial boards

Personnel Commitments for FY 2007:
D. J. Singh (40%); R. S. Fishman (60%); F. A. Reboredo 100(%), Z. Zhang (40%); S. Okamoto (90%); E. Dagotto, ORNL UT Distinguished Scientist (50%); A. Moreo, ORNL/UT Joint Faculty (50%); A. Eguiluz, ORNL/UT Joint Faculty (40%); S. Pantelides, Vanderbilt Distinguished Scientist (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 BA $1575K **FY 06 BA** $1780K **FY 07 BA** $2180K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01 0

FWP: Chemistry of Advanced Inorganic Materials

FWP Number: ERKCC01

Program Scope: The goal of this program is to discover controlled synthetic methods to produce and characterize novel inorganic nanometer-scale materials and to gain a fundamental understanding of how nanoscale dimensions impact physical and chemical properties. To realize this goal, we carry out two synergistic tasks. In the first, we focus on three specific questions: How do intermolecular interactions and the forces of self assembly dictate the properties of oriented nanostructures?; How are the physical and functional properties of oriented thin film materials adjusted using chemical solution and vapor deposition methods?; What is the effect of reduced dimensionality (for example, how behavior changes when gases and fluids are confined at surfaces/interfaces or entrained in porous media with nanometer scale architectures)? In the second task, we investigate the adsorption of hydrogen and hydrogen-bearing small molecules onto or within porous oxide media synthesized under the first task. To address these two tasks, we use a combination of synthesis, neutron scattering and advanced modeling to aid discovery and development of a quantitative, molecular level description of molecule-molecule and molecule-surface interactions.

Major Program Achievements: Neutron diffraction and high resolution thermodynamic adsorption investigations have been employed to characterize the layering behavior of n-hexane, n-butane and n-pentane thin films on MgO(100) surfaces. The structure of a monolayer film of several alkanes (i.e., n-butane, n-pentane, n-hexane) was determined with *unrivalled* accuracy; *Ab initio* molecular modeling and high resolution inelastic neutron scattering (INS) studies of the low temperature rotational motion of CH_4 thin films on MgO(100) surfaces were combined to demonstrate that CH_4 adsorbs with the two fold axis perpendicular to the (100) plane; Understanding of the growth of solution derived films has led to the improvement of solution buffers compared to that of the underlying metal substrate (e.g., solution grown La_3NbO_7 films with improved texture); The structure and dynamics of molecular H_2, HD and D_2 films on MgO (100) surfaces and within porous carbon materials were determined using neutron diffraction, INS, thermodynamics and molecular modeling. The binding energy and rotational motion was incorporated in a model (using realistic potentials) to show that hydrogen is adsorbed above the Mg^{2+} at low densities and are displaced from those positions as the surface density and film thickness increase.

Program Impact: Understanding of fundamental aspects of synthesis and the dynamics and mechanisms of reactions at interfaces as well as the relationship between properties and nanoscale dimensions will have significant impact in the areas of materials chemistry and nanoscience and technology.

Interactions:
Internal–This work will impact, and benefit from, other BES projects in geochemistry (ERKCC51 and ERKCC52), polymer science (ERKCC02), epitaxial complex oxides (ERCKS80), superconductivity (ERKCS82), nanomaterials (ERKCT08), surface chemistry related to heterogeneous catalysis (ERKCC43), and computational chemical sciences (ERKCE09).
External–University of Delaware; Cambridge University and BP Institute; University of Southern Georgia; University of Madrid; University Lund; ISIS; Cambridge University; University of Cincinnati; University of ; University of Tennessee

Recognitions, Honors and Awards:
M. Paranthaman: Editorial Board, Associate Editor, *J. Amer. Ceram. Soc.*; Editorial Board, *Superconductor Sci. Technol*; M. Hu: Editor-in-Chief, *J. Nanomaterials*; J. Z. Larese: Panel participant, Swedish Research Council subcommittee for the European Spallation Source; keynote lecture at the European Conference on Neutron Scattering, June 2007

Personnel Commitments for FY2007:
M. Paranthaman (20%), and M. Z. Hu (30%), J. Z. Larese, ORNL/University of Tennessee Collaborating Scientist (50%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY05 BA $990K **FY06 BA** $1025K **FY07 BA** $1025K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01 0

FWP: Polymer-Based Multicomponent Materials

FWP Number: ERKCC02

Program Scope: Combining experimental, theoretical and synthetic approaches, we perform fundamental studies of the structure, dynamics and thermodynamics of macromolecular systems to provide a better understanding of the macroscopic properties of advanced polymeric materials. Major experimental tools include synthesis, X-ray and neutron scattering, NMR spectroscopy, electron and optical microscopies. Simulation and theoretical approaches include molecular dynamics, Monte Carlo, mean field, lattice, and integral equation theory.

Major Program Achievements: Quantification of the dispersion of polystyrene grafted silica particles in lamellar forming polystyrene-polybutadiene diblock copolymers. Phase behavior was evaluated over molecular weights spanning 34,000 g/mol to over 1,000,000 g/mol resulting in new and unanticipated principles for creating homogeneous nanocomposites. Synthesis and characterization of various forms of saturated hydrocarbon multiblock copolymers produced by catalytic hydrogenation of polystyrene and polydiene based compounds. Shear alignment and mechanical testing revealed complex mechanisms of failure in ABA triblock and ABCBA pentablock copolymers. Synthesis and characterization of crosslinked polymer nanoparticles of varying crosslinked density; studies of dispersions of these nanoparticles by SANS. Design, synthesis and characterization of ABCA and ABAC tetrablock copolymers containing poly(cyclohexylethylene), poly(ethylene-co-propylene), and poly(dimethylsiloxane) for the purpose of producing mechanically robust nanoporous materials. A detailed quantum investigation of the nature of the interactions between individual chemical functional groups and nanotubes carried out in order to rationally design future generations of nanocomposite materials. The morphologies (both 2 and 3D) for branched diblock (AB) copolymers were elucidated by using self consistent field theory and varying the branch point between two polymers (PMMA and PS) while keeping the volume fractions constant. A complete morphology phase diagram was computed with good agreement with large scale molecular dynamics simulations. Further simulations have explored how to fine tune the size and packing of the hexagonal cylindrical phases. Electronic structure and dynamics in combination with experiments was used to determine the underlying mechanism responsible for the growth of bamboo-like nanotubes and for highly branched nanotubes. In addition the electronic properties of exohedrally doped double walled nanotubes was elucidated using high-level quantum calculations in combination with Raman spectroscopy studies.

Program Impact: Provides insights on the microscopic origins of macroscopic properties of polymer solids, melts, blends, alloys and composites, co-polymers, micellar systems, and small molecule analogs. Results have significant impact on the physics, chemistry and synthesis of polymers, the structure and dynamics of polymers, and the statistical mechanics and simulation of macromolecular systems.

Interactions:
National Laboratories: ANL, LANL, LLNL, NIST, Sandia; National and international user facilities: CNMS, HFIR, IPNS, APS, NCNR, LANSCE, ISIS, Risø, Forschungszentrum (Juelich), Saclay; Universities: collaborations/interactions with over forty US and foreign universities and over 10 companies.

Recognitions, Honors and Awards:
45 invited presentations in FY 2007; Four APS Fellows; one National Academy of Engineering member; MRS David Turnbull Lectureship Award; two APS High Polymer Physics Prize winners; two APS Dillon Medals; former president Neutron Scattering Society of America; Distinguished Scientist/Professor; Chair 2007 Polymers West Gordon Research Conference: two Chairs of APS Polymer Physics Division; Arnold Beckman Award; two ACS Doolittle Awards, 2008 ACS Collaborative Research Award; numerous regional, national, international advisory committees; editorial/advisory boards.

Personnel Commitments for FY 2007:
J. W. Mays, ORNL/UT Distinguished Scientist (50%), B. G. Sumpter (30%), V. Urban (20%), K. S. Schweizer, University of Illinois (10%), S. W. Sides, TX Corp. (30%), F. S. Bates, University of Minnesota (10%), M. D. Dadmun (10%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY05 BA $1785K **FY06 BA** $ 1485K **FY07 BA** $1485K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01 0

FWP: Materials for Catalysts

FWP Number: ERKCS05

Program Scope: Explore the synthesis, near-surface properties, and chemical activity of support materials for heterogeneous catalysis. Investigate unique compositions, structures, and combinations of materials that can only be achieved by vapor deposition synthesis. Elucidate the interactions between the catalyst and support material including the defect composition and mobility, the space charge segregation, and the atomic structure at the support-catalysts interface. Characterize the catalytic activity with simple, but relevant reactions of small molecules. Utilize ORNL's unique high resolution electron microscopy to investigate structural properties.

Major Program Achievements: Catalyst particles have been vapor deposited onto a tumbling, high-surface-area powder support. This novel process offers a number of practical and scientific advantages compared to the commonly used solution synthesis techniques. In particular, vapor deposition eliminates all sources of contamination associated with chemical precursors. It also greatly expands the selection of compositions for both the particle and support materials for detailed scientific studies. Unexpected variation in the reactivity of 2 to 3 nm gold nanoparticles related to the composition and crystal phase of the ceramic support is providing new insight. Gold nanoparticles have been formed on silica, tungsten oxide, carbons, boron compounds, and chemically modified titanium oxides. The particle size, catalytic activity, and thermal stability of the particles on different support materials have been correlated with potential energy calculations. High-resolution *Z*-contract electron microscopy has identified dispersed single atoms in addition to the nanometer-sized clusters and has confirmed deactivation due to thermal and light enhanced coarsening. Thin-film samples have been deposited and studied to complement studies of powder-supported catalysts. The planar form offers better control of composition and deposition conditions, and facilitates characterization of the electrical, electrochemical, and optical properties of the supported catalyst. In addition, co-deposition of both the support and catalyst phases using oblique-angle sputter deposition produces catalysts with sufficiently high surface area to characterize in small batch reactors.

Program impact: Has provided new perspective on the important field of catalysis where inorganic materials serve as both catalysts and active support materials.

Interactions:
Internal– Electron Microscopy Group, Surface Chemistry and Catalysis Group, Materials Science and Technology Division; Computer Science and Mathematics Division
External–Idaho National Laboratory; University of Milan; Argonne National Laboratory; University of Virginia; University of Tennessee; Battelle Columbus; Tennessee Technological University; University of Maryland; MIT; Wake Forest University; World Gold Council and Mintek, South Africa

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
4 invited presentations in FY 2007; National Federal Laboratory Consortium Award of Excellence in Technology Transfer, 2004

Personnel Commitments for FY 2007:
N. J. Dudney (40%); G. Veith (90%)

Authorized Budget (BA) for FY 05, FY 06, FY 07:
FY 05 BA $660K **FY 06 BA** $560K **FY 07 BA** $560K