

Solid State Nanoscience
Chemical Physics Workshop 2004

University of Tennessee, Knoxville

ABSTRACTS

Quantum Tunneling of the Magnetization in Molecular Nanomagnets

Myriam Sarachik
City University of New York

Molecular nanomagnets, sometimes referred to as single molecule magnets, have attracted a great deal of recent attention for interesting behavior that is borderline between the classical and quantum mechanical regimes, and because of their potential usefulness for high-density data storage and quantum computation. Quantum mechanical processes are observed in these materials on a macroscopic scale in the form of steps in the magnetization curves. Typical behavior of the class will be examined by considering Mn₁₂-acetate, a particularly simple prototype.

Ferroelectricity in Ultra-Cold Free Metal Clusters: A Precursor to Superconductivity

Walt de Heer

Georgia Institute of Technology

Electric deflections of gas-phase, cryogenically cooled neutral niobium clusters (Nb_N , $N=2-150$, $T=20-300$ K), measured in molecular beams, show that specific cold clusters attain an anomalous component with very large electric dipole moments. In contrast, room temperature measurements show normal metallic polarizabilities. Characteristic energies $k_B T_c(N)$ are identified below which this ferroelectric-like state develops. Generally, T_c decreases ($110 > T_c(N) > 10$ K) as N increases with pronounced even-odd alternations for $N > 38$. Similar effects are observed in Ta_N and V_N but not in Mn_N , Co_N , Bi_N , suggesting a connection between this novel state of metallic matter and bulk superconductivity.

From Molecular Nanomagnets to Interactive Quantum Qubits

Bruce Harmon

Iowa Stats University and AMES Laboratory

The ground state and excited state collective spin configurations in molecular nanomagnets present a great challenge for first principles electronic structure calculations. The calculated and empirically determined exchange interactions can be used to explore dynamical properties using model Hamiltonians. Quantum spin tunneling, and the decoherence of interacting qubits as a result of random spin baths will be considered.

Exchange Biased Nanostructures || Friday 11:00 - 12:00 pm , 511 Buehler , UT.

Ivan Schuller
University of California , San Diego.

Magnetic nanostructures are receiving increasing attention in recent years, motivated by the interesting phenomena when the physical size becomes comparable to relevant magnetic length scales. In addition a number of important potential applications in the sensors and storage industries have emerged. When magnetic nanostructures are in contact with other dissimilar magnetic materials and because their magnetic fields extend considerably outside the physical structure they are very susceptible to interactions with the surrounding environment. A particularly interesting situation is one in which a ferromagnetic nanostructure is in contact with an antiferromagnetic substrate. In this "exchange biased" configuration, a variety of unusual phenomena arise; the reversal mode of the ferromagnet changes considerably, the superparamagnetic transition temperature is affected and there is a noticeable change in the microscopic spin configuration. I will describe a series of experiments in which we studied these phenomena in nanostructured ferromagnets prepared by electron beam lithography and self assembly.

Inorganic Nanotubes and Inorganic Fullerene-Like Materials from Layered Compounds: From Concept to Applications

Reshnef Tenne
Weizmann Institute

We have proposed that nanoparticles of layered compounds will be unstable against folding and close into fullerene-like structures and nanotubes (*IF*). Initially this hypothesis was realized in WS_2 and MoS_2 . Subsequently, nanotubes and fullerene-like structures were prepared from numerous compounds of layered structure by various groups. Much progress has been achieved in the synthesis of inorganic nanotubes and fullerene-like nanoparticles of WS_2 and MoS_2 and many other metal dichalcogenides over the last few years. Synthetic methods for the production of multiwall WS_2 nanotubes by sulfidizing WO_3 nanoparticles have been described and further progress is underway. A fluidized-bed reactor for the synthesis of up to 70 g of fullerene-like WS_2 nanoparticles has been established and scale-up of the synthesis to pilot industrial production is under way. The detailed mechanisms for the synthesis of fullerene-like WS_2 and MoS_2 nanoparticles and nanotubes of these compounds have been elucidated. The synthesis and the structure of various *IF* materials from metal-dihalides will be discussed as well. Hydrothermal synthesis proves to be a very efficient strategy to synthesize macroscopic amounts of inorganic nanotubes of various sorts.

Substantial progress has been achieved in the use of such nanoparticles for tribological applications. Few testing programs have been undertaken together with industrial partners and have clearly indicated the usefulness of the fullerene-like WS_2 (MoS_2) as solid lubricants in various products. Some of these applications will be briefly described. Other potential applications, for example in high strength nanocomposites; catalysis and rechargeable Li batteries, will be discussed as well.

Clusters, Nanoparticles and Filaments from the Vapor Phase: Synthesis, Structures and Reactions

Samy El-Shall

Virginia Commonwealth University

The study of gas phase clusters provides information on how the properties of matter evolve as the size of a material system ranges from molecular to macroscopic dimensions. In this work, we investigate the structures of benzene cluster cations $[(C_6H_6)_n]^+$ and the solvation of atomic metal cations within benzene clusters $[M+(C_6H_6)_n]$ using a combination of ion mobility experiments and theoretical calculations. For the benzene cluster cations, two different growth patterns involving a sandwich dimer core or a pancake trimer stack core have been identified. The lowest energy isomers of the $n = 3-6$ clusters incorporate the pancake trimer stack as the cluster's core. The trimer stack allows the charge to hop between two dimers, thus maximizing charge resonance interaction in the clusters. For larger clusters, the appearance of magic numbers at $n = 14, 20, 24, 27$ and 30 is consistent with the incorporation of a sandwich dimer cation within icosahedral, double icosahedral, and interpenetrating icosahedral structures. Several metal cations such as Ti^+, V^+, Fe^+ and Ni^+ show a strong tendency to form sandwich structures with two benzene molecules and exhibit preference solvation by 14 benzene molecules in the $M+(C_6H_6)_n$ clusters. The interpretation of these results in view of the proposed structures and the growth patterns of the clusters will be presented.

In the nanoparticle research, we will present a method to synthesize size-selected nanoparticles of a variety of materials by coupling the laser vaporization controlled condensation (LVCC) technique with a differential mobility analyzer (DMA). The LVCC method is based on using pulsed laser vaporization within well-defined conditions of temperature and pressure in a cloud chamber. The LVCC method can be coupled to plasma and ionic polymerization techniques, thus allowing the incorporation of metallic nanoparticles within polymer films. We will present the application of the LVCC method for the catalysis of gas phase polymerization of several olefin monomers. Finally, the assembly of the nanoparticles into filaments and fibers in the gas phase induced by an electric field will be presented and discussed. The results have significant implications for the ductility and the plastic behavior of the materials formed from consolidated nanoparticle assemblies.

Molecular Simulation of the Structure and Rheology of Nanoconfined Fluids

Peter Cummings
Vanderbilt University

Over the past decade, our research group has been involved in performing molecular dynamics simulations of nanoconfined fluids, both at rest and under applied shear rates. We have simulated linear alkanes, branched alkanes and, more recently, water. Here we review our work and compare with experimental measurements. We are particularly interested in transitions between fluid and ordered states under nanoconfinement.

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In situ Measurements of Carbon Nanotube Growth Kinetics - The Race to Nanotube-Based Composites BA

David Geohegan
Oak Ridge National Laboratory

Despite the relative ease with which carbon nanotubes can be synthesized, controlling and optimizing their growth constitutes a grand challenge in nanoscience. Precise control of nanotube length and electronic properties are essential for their application in electronic devices or sensors while understanding how to grow long nanotubes at high rates is a major production challenge for their use in composites. Recent in situ measurements of nanotube growth kinetics will be described which have permitted the repeatable synthesis of millimeters-long mats of vertically-aligned multiwall carbon nanotubes (VA-MWNT) on prepatterned metal catalyst films for use in multifunctional nanotube-polymer composites. Time-resolved laser reflectivity is used to measure nanotube lengths and rates of growth to heights of the first few microns, while direct imaging using remote microscopy is utilized to directly photograph the growth to millimeters heights. These kinetics measurements provide some of the first valuable input to growth models designed to predict when and why nanotube growth terminates, and how to prolong growth to even longer lengths - at high rates. Growth kinetics of single-wall carbon nanotubes by laser vaporization will be reviewed and compared. Uses of carbon nanotubes in polymer composites and challenges in measurements technology to assess their enhancements in thermal conductivity, electrical conductivity, strength, and other functionalities will be discussed.

Seeing the atoms more clearly: the impact of aberration-corrected STEM on nanoscience

Steve Pennycook
Oak Ridge National Laboratory

Aberration-correction is currently one of the most exciting developments in electron microscopy, doubling the achievable resolution and enormously improving image contrast and quality. It is now possible to image *individual* atoms inside materials or on their surfaces, and through electron energy loss spectroscopy, to identify them and probe their local electronic environment. Oak Ridge National Laboratory has two of the first such corrected microscopes, and recent insights will be presented from several areas of nanoscience, including nanoscale phase separation in “highly-correlated” oxides, La-stabilization of γ -alumina for catalyst supports, and the activity of gold and semiconductor nanocatalysts. Future prospects for three-dimensional atomic-resolution tomography will be discussed.

Long Range Order of Nickel Nano-Dots Templated by Self-Assembled Diblock Copolymer Thin Films using Graphoepitaxy

Scott Fontana
University of Tennessee

Controlling the interfacial energies and wetting behavior of asymmetric diblock copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA) in contact with a silicon surface, enables us to control the orientation of its micro-phases. The micro-phases of the diblock copolymer that are placed onto a neutral surface will align perpendicularly to the surface. Neutrality is obtained when there is no preference for one of the blocks to segregate to an interface. This is achieved by a variety of different methods. One of the methods for achieving neutrality is to passivate the surface of the silicon wafer. This is done by removing the silicon oxide layer from the wafer with a washing of hydrofluoric acid solution.

A diblock copolymer thin film, of a controlled thickness, that is cast onto a neutral surface will micro-phase separate and align perpendicular to the surface. The film must have a thickness that is $\sim L_0$ and be annealed above its T_g for a set time allowing the micro-phases to align. By controlling the ratio of PS to PMMA the micro-phase morphology can be controlled. When the minor phase of a diblock copolymer is $\sim 22\%$, hexagonally close packed cylinders form. PMMA cylinders can easily be degraded with 254 nm UV radiation and removed from the polymer matrix by washing with acetic acid leaving a nanoporous template.

Published work has shown that graphoepitaxy provides a method for achieving long-range order of spherical domain block copolymers. This ordering is obtained by confining the micro-phases on mesas and in wells of a patterned substrate to achieve long range alignment over a sample. The goal of this research is to combine the work being done on vertically aligned diblock copolymer systems and graphoepitaxy to achieve long-range order of vertically aligned diblock copolymer films.

These long-range ordered and vertically aligned diblock copolymer films can be used as a template to produce arrays of nickel nanodots. Nickel is deposited onto the copolymer template, covering the polymer matrix as well as partially filling the pores. The polymer matrix can be lifted off along with the overlaying Nickel producing an array of Ni nanodots. From these ordered nanodots, carbon nanofibers can be grown using PECVD growth conditions. The result is a highly ordered carbon nanofiber array that has potential uses in quantum electronics and optics.

Magnetic Excitations in Weakly Interacting Spin Clusters : Saturday 11:00 - 11:30 pm , 511 Buehler , UT.

**Steve Nagler
Oak Ridge National Laboratory**

In this talk I will review some basic features of excitations in weakly interacting or isolated spin clusters. The systems under consideration range from simple magnetic dimers to larger members of the single molecular magnetic materials. In particular I will discuss the role of inelastic neutron scattering illustrated by several examples.

**Superconductivity, Spin Density Waves and Charge Ordering on a Quasi-2d
Triangular Lattice: $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$**

Brian Sales

Oak Ridge National Laboratory

Crystal structure, magnetic susceptibility, electrical and thermal transport, and heat capacity data are reported for single crystals (from floating zone growths) and polycrystalline samples of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($0.35 < x < 0.75$, $0 < y < 1.4$). The evolution of the various physical properties with variable sodium and water content will be presented and discussed. Particular emphasis will be placed on separating the intrinsic properties of these materials from effects due to impurity phases and disorder. The measured electronic and magnetic properties of these materials will be compared to those expected from electronic structure calculations (D. Singh and others). Evidence for strong electronic correlations based on the normal state properties of the sodium cobaltates also will be discussed.

Synthesis of One-Dimensional Functional Nanomaterials: Chemistry Approach

Sheng Dai
Oak Ridge National Laboratory

Two central challenges in nanoscale science and technology are, first, to develop efficient methods for synthesizing high quality nanomaterials with well-controlled properties, and, second, to direct their assembly from the nanoscale upward into functional configurations. Control of nanomaterials properties generally requires synthesis of only a narrow size distribution, while functional assembly usually implies controlling the location and/or the orientation of the nanomaterials. It must be emphasized that the directed assembly requirement cannot be met at this time by even the highest resolution electron beam lithography, for both technical and economic reasons. Consequently, successful syntheses often will require spatially confining and self-assembly growth of nanoscale structures. This talk will be focused on chemistry approach toward the efficient synthesis and replication of one-dimensional materials. The various growth methodologies developed at our research group for synthesizing such key building block in nanotechnology will be discussed.

**Thermodynamic and Neutron Studies of Ethane Thin Films on MgO(100) :
Saturday 1:30 - 2:00 pm , 511 Buehler , UT.**

Rick Cook
University of Tennessee

The adsorption properties of ethane on MgO (100) surface were studied using neutron scattering and volumetric isotherm techniques. A series of adsorption isotherm measurements were performed between 100 K and 140 K using an automated high-resolution adsorption apparatus. These data were used to determine both the two-dimensional isothermal compressibility and the isosteric heat of adsorption. We find evidence for the presence of at least three layering transitions. Earlier studies suggest that two solid monolayer phases of different densities form on the MgO(100) surface. We present our preliminary investigations of these monolayer solid phases using neutron vibrational spectroscopy. Some preliminary indications of the nature of the dynamical properties of these solid phases will be presented by making comparisons of the neutron spectra with calculations of the molecular vibrational modes. Finally, comparisons of our investigations and findings with earlier experimental measurements will be included.

Oriented Semiconducting Polymer Nanorods: New Insights Into Luminescence from Conjugated Polymer Nanostructures

Adosh Mehta

Oak Ridge National Laboratory

Conjugated polymers have attracted tremendous attention in recent years due to their potential applications in the area of optoelectronics and photonics. Recent work in our laboratory has demonstrated a technique to deposit oriented rod-like nanostructures from single molecules of conjugated polymers. These nanostructures exhibit extraordinary photostability and unique spectroscopic properties in ambient conditions. We have used a combination of techniques such as far field fluorescence and scanning probe microscopy, single molecule spectroscopy, and molecular mechanics simulation to understand the structure and luminescence properties of these nanoparticles. Recent results detailing the photophysics and intramolecular order of these polymer nanorods will be discussed. These results suggest exciting applications of these nanostructures in the area of molecular-optoelectronics and nanoscale photonics.

Metallic "Ferroelectricity" in the Pyrochlore $\text{Cd}_2\text{Re}_2\text{O}_7$

Dave Mandrus
Oak Ridge National Laboratory

Structural phase transitions characteristic of ferroelectricity are not expected in metals because the itinerant electrons in a metal screen the long-range electrostatic forces responsible for these transitions. Fundamentally, however, there is nothing preventing a "ferroelectric" structural phase transition in a metal, and this scenario was first discussed by P.W. Anderson and E. I. Blount (A&B). However, because no materials were found that obeyed A&B's criteria, ideas regarding "ferroelectric metals" have not been pursued over the past 38 years. Here we present measurements of the elastic moduli of the pyrochlore $\text{Cd}_2\text{Re}_2\text{O}_7$ through the 200 K cubic-to-tetragonal structural phase transition 2-6 that show that this transition is "ferroelectric" in the structural sense described by A&B. We also present first-principles calculations of the lattice instabilities. These calculations indicate that the dominant lattice instability corresponds to a two-fold degenerate mode with Eu symmetry, and that motions of the O ions forming the O octahedra dominate the energetics of the transition. We conclude that the coupled structural/electronic transition at 200 K in $\text{Cd}_2\text{Re}_2\text{O}_7$ is a qualitatively new continuous phase transition in a solid.