

**Chemistry and Materials Science
Directorate 2003 Postdoctoral Symposium**

A. Arsenlis

July 16, 2003

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

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Chemistry and Materials Science Directorate

2003 Postdoctoral Symposium

July 16, 2003



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2003 Chemistry and Materials Science Postdoctoral Program Symposium
 Wednesday, 16 July 2003
 B235, Gold Room

TALKS

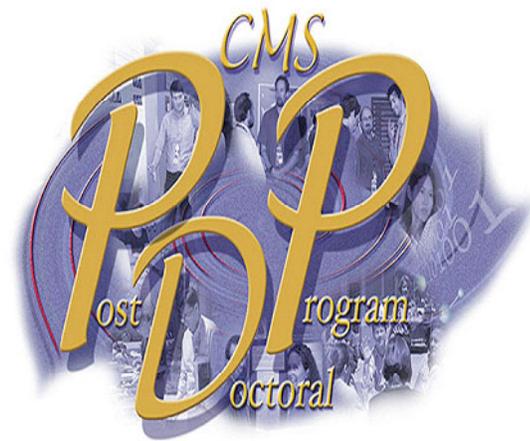
| | | |
|--------------|---------------------------|---|
| 9:00 AM | Welcome and Introductions | Tom Arsenlis, CMS Postdoc Program |
| 9:05 | Olgica Bakajin | “Carbon Nanotube-Based Microfluidic Elements, Membranes and Sensors” |
| 9:25 | Herb Tobias | “Determination of the Metabolic and Physiochemical State of Individual Bacterial Cells” |
| 9:45 | Brad Hart | “Laser-Initiated Nanoscale Molecularly-Imprinted Polymers” |
| 10:05 | Tony Esposito | “Analysis of Individual Cells and Endospores by Micro-Raman Spectroscopy” |
| 10:25 | BREAK | Poster Session – B235 Lobby |
| 11:00 | Wei Cai | “Dynamic Transitions in Dislocation Motion: From Smooth to Rough to Twinning” |
| 11:20 | Jonathan Crowhurst | “Implusive Stimulated Light Scattering Under Extreme Conditions” |
| 11:40 | Barry Cheung | “Assembly of Virus Arrays on Templates of Chemoselective Linkers Formed by Scanning Probe Nanolithography” |
| 12:00 | Sergei Kucheyev | “Ion-Irradiation-Produced Disorder in Wide Band-Gap Semiconductors” |
| 12:30 | LUNCH | B235 Patio |
| 1:30 | Poster Session | B235 Lobby |
| 3:00 | Brady Clapsaddle | “Silicon Oxide in Metal Oxide Matrices: Synthesis, Characterization, and Applications as Energetic Nanocomposite Materials” |
| 3:20 | Erik Nelson | “Determination of Iodine Speciation in Environmental Samples Using X-ray Absorption Spectroscopy” |
| 3:40 | Lucian Mihailescu | “A 4π Camera for Gamma-Rays” |
| 4:00 | Tom Trelenberg | “The Properties of Actinide Nanostructures” |
| 4:20 | Adjourn | |

POSTERS

| | |
|-------------------|--|
| Kerri Blobaum | “Investigating the δ to α' Martensitic Phase Transformation in Pu-Ga Alloys” |
| Christoph Bostedt | “Electronic Structure and Surface Passivation Effects of Group IV Semiconductor Nanocrystals” |
| Julio Camarero | “Methods for Oriented Attachment of Virus and Protein Arrays using a Combination of Chemo-Selective Ligation Methods and Nanolithography Techniques” |
| Sarah Chinn | “Advances in High Sensitivity Microcoil NMR” |
| Wonyoung Choe | “Enhancing Magnetostriction by Exchange-Coupling in Magnetic Nanoparticles” |
| Keith Coffee | “A High Efficiency Highly Selective Biological Aerosol Monitoring System” |
| David Ferguson | “Reagentless Real-Time Identification of Individual Microorganisms by Bioaerosol Mass Spectrometry” |
| Stephen Glade | “Positron Annihilation Spectroscopy and Small Angle Neutron Scattering Characterization of Nanostructural Features in Irradiated Fe-Cu-Mn Alloys” |
| Aaron Golumbfskie | “A Three-Dimensional Model of Intercellular Signaling in Epithelial Cells” |
| Julie Herberg | “Investigation of Ti-Doped NaAlH ₄ by Solid-State NMR” |
| Masato Hiratani | “Stochastic Dislocation Dynamics Simulations of Plastic Deformation in Irradiated Metals” |
| Andrea Hodge | “Nanomechanical Behavior of Multi-Component Metastable Materials” |
| Tina Jayaweera | “Suppression of a Premixed C ₃ H ₈ -Air Flame by Halogenated and Phosphorus-Containing Compounds” |
| I-Feng W. Kuo | “Structures and Dynamics of Air-Water Interface from <i>ab initio</i> Molecular Dynamics” |
| Scott McCall | “Anisotropy Revealed in a Magnetic Field: A Study of Single Crystal Ca ₃ Ru ₂ O ₇ ” |

POSTERS (continued)

| | |
|-------------------|---|
| Robert Meulenberg | “Electronic Structure and Surface Physics of Quantum Dots” |
| Taira Okita | “Standard Rate-Theory Predictions of Irradiation Damage Evolution in Comparison with Microstructural Data” |
| Josh Patin | “The Search for Superheavy Elements: The Discoveries of Elements 114 and 116 and Initial Results for Element 118” |
| Josh Patin | “Random Probability Analysis of the $^{48}\text{Ca} + ^{249}\text{Cf}$ Experiment” |
| Roger Qiu | “Molecular Mechanisms of Kidney Stone Inhibition by Proteins and Small Molecules” |
| Tim Ratto | “Double-Tethered Force Spectroscopy of the Concanavalin A Mannose Bond” |
| Bryan Reed | “Aloof Transmission Electron Energy-Loss Spectroscopy and its Application to Nanostructures” |
| Bahrad Sokhansanj | “Modeling <i>Yersinia pestis</i> Systems Biology” |
| Herbert Tobias | “Determination of the Metabolic and Physiochemical State of Individual Bacterial Cells” |
| Anh-Tuyet Tran | “Structural Determination of Myelin Oligodendrocyte Glycoprotein Using Nuclear Magnetic Resonance Methods” |
| Luis Zepeda-Ruiz | “Structure, Energy and Mobility of Self-Interstitial Dislocation Loops in Vanadium” |
| Alex Ziegler | “Effects of Grain Boundary Constraint on the Constitutive Response of Tantalum Bicrystals” |



*Abstracts Are
Arranged Alphabetically*

CARBON NANOTUBE-BASED MICROFLUIDIC ELEMENTS, MEMBRANES AND SENSORS

Olgica Bakajin¹, A. Artyukhin¹, N. Ben-Barak², D. Eagleham³, J. Grossman⁴,
G. Galli Gygi⁴, A. Noy², J. Peng²

¹University Relations Program, LLNL

²Chemical Biology & Nuclear Science Division, LLNL

³CMS Associate Director Office, LLNL

⁴H Division, LLNL

Abstract

Olgica Bakajin¹, N. Ben-Barak², J. Peng², D. Eagleham³, J. Grossman⁴,
G. Galli-Gygi⁴, A. Noy²,

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Abstract

I will discuss recent progress in two projects that I am working on that all involve use of carbon nanotubes.

Firstly, we have developed a method for integration of patterned arrays of carbon nanotubes into microfabricated channels. I will describe a carbon nanotube filtering devices fabricated using this method and discuss the use of carbon nanotube arrays as molecular concentration and separation media. The fundamental chemical force microscopy studies of interactions of nanotubes with different chemical groups, in combination with *ab-initio* modeling will allow us to apply rational design to the separation and concentration systems.

In the second project we are embedding ordered nanotubes in a thin film to make a semi-permeable membrane with ideal pores. With this architecture we are hoping to observe often modeled but not yet observed molecular transport through the nanotubes and create chemically selective membranes with pore diameters commensurate with the size of macromolecules. I will also discuss design and fabrication of a single nanotube nanotunnel.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

INVESTIGATING THE δ TO α' MARTENSITIC PHASE TRANSFORMATION IN Pu-Ga ALLOYS

Kerri Blobaum¹, Jeff Haslam¹, Mark Wall¹, Adam Schwartz¹

¹Materials Science and Technology Division, LLNL

Abstract

The δ/α' phase transformation in Pu-Ga alloys is scientifically interesting and not well understood. On cooling below ~ 150 K, the ductile fcc δ phase partially transforms to a two-phase microstructure consisting of the brittle monoclinic α' phase in δ phase. The α' phase has a 20% smaller volume and a 30% larger resistivity. This transformation is believed to be martensitic, and, depending on composition, the maximum amount of α' formed is about 30%. The austenitic reversion to δ does not begin until the alloy is heated to ~ 320 K. Using several characterization techniques including microscopy, resistometry, and differential scanning calorimetry, we are probing the thermodynamics and kinetics of this transformation to better understand why it has such a large hysteresis and why the δ phase only partially transforms to α' . Resistivity experiments on a 0.6 wt% Pu-Ga alloy showed reproducible martensite start and austenite start temperatures during thermal cycling (154 K and 310 K, respectively). Isothermal annealing indicated a possible incubation period for the transformation. Using differential scanning calorimetry, the δ to α' transformation was observed on cooling, and the heat of transformation was measured as a function of cooling rate and prior thermal cycling. On heating, differential scanning calorimetry traces showed an unusual periodic series of spikes corresponding to the α' to δ reversion. It is possible that this is indicative of a burst transformation mechanism. Initial results indicated that the transformation temperatures observed with differential scanning calorimetry correlated well with recent resistivity results and prior dilatometry work by other groups.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ELECTRONIC STRUCTURE AND SURFACE PASSIVATION EFFECTS OF GROUP IV SEMICONDUCTOR NANOCRYSTALS

C. Bostedt¹, T. van Buuren¹, T. Willey², and L. J. Terminello³

¹Material Science and Technology Division, LLNL

²University Relations Program, LLNL

³CMS Associate Director Office, LLNL

Abstract

With nanostructured materials one can manipulate and control the properties of a material through the fabrication of nanometer scale structures. Tailoring the electronic properties of nanostructures is often achieved by confining electrons to dimensions comparable to their wavelength, which leads to quantum well states that modify the density of states. Until recently, the effect of the surface layer on the electronic and structural properties of the quantum dots has been neglected due to the inherent difficulty in both modeling and measuring this region.

X-ray absorption (XAS), soft x-ray emission (SXE), and photoemission (PES) spectroscopy have been performed on diamond, silicon, and germanium nanocrystals. Clean Ge nanocrystal films are found to exhibit much stronger quantum confinement effects at the band edges than in similar-sized Si and diamond particles. This effect leads to a critical particle size of 2.2 nm below which the band gap of Ge becomes larger than that of Si. Additionally our experimental results show how the surface of bare nanocrystals is reconstructed, and specific reconstruction mechanisms are identified. Surface passivation of the nanoparticles is found to strongly alter the overall electronic properties of these quantum dots. These findings are compared to state-of-the-art electronic structure calculations.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

DYNAMIC TRANSITIONS IN DISLOCATION MOTION: FROM SMOOTH TO ROUGH TO TWINNING

Wei Cai¹, Jaime Marian², Vasily V. Bulatov³

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²California Institute of Technology, Pasadena, CA

³Materials Science and Technology Division, LLNL

Abstract

First observations of the long-hypothesized kink-pair mechanism in action are obtained in atomistic simulations of dislocation motion in iron. However, in a striking deviation from the classical picture, dislocation motion under higher stress becomes rough resulting in spontaneous self-pinning and production of large quantities of debris. Then, under still higher stress, the dislocation stops abruptly and emits a twin plate that immediately takes over as the dominant mode of plastic deformation. These observations challenge the applicability of the Peierls threshold concept to 3-dimensional motion of screw dislocations and suggest a new interpretation of plastic strength and microstructure of shocked metals.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

METHODS FOR ORIENTED ATTACHMENT OF VIRUS AND PROTEIN ARRAYS USING A COMBINATION OF CHEMO-SELECTIVE LIGATION METHODS AND NANOLITHOGRAPHY TECHNIQUES

Julio A. Camarero

University Relations Program, LLNL

Abstract

The present work describes our ongoing efforts towards the creation of nano-scaled ordered arrays of protein/virus covalently attached to site-specific chemical linkers patterned by different nanolithography techniques. We will present a new and efficient solid-phase approach for the synthesis of chemically modified long alkyl-thiols. These compounds can be used to introduce chemoselective reacting groups onto gold and silicon-based surfaces. Furthermore, these modified thiols have been used to create nanometric patterns by using different nanolithography techniques. We will show that these patterns can react chemoselectively with proteins and/or viruses that have been chemically or recombinantly modified to contain complementary chemical groups at specific positions thus resulting in the oriented attachment of the protein or virus to the surface. Also, a total novel and generic approach for the chemo-enzymatic and photo-switchable attachment of proteins to surfaces will be presented.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ASSEMBLY OF VIRUS ARRAYS ON TEMPLATES OF CHEMOSELECTIVE LINKERS FORMED BY SCANNING PROBE NANOLITHOGRAPHY

Chin Li Cheung¹, Julio A. Camarero², Bruce W. Woods³, Jim J. De Yoreo¹,
Tianwei Lin⁴, John E. Johnson⁴

¹ Chemical Biology & Nuclear Science Division, LLNL

² University Relations Program, LLNL

³ New Technologies Engineering Division, LLNL

⁴ The Scripps Research Institute, Dept. of Molecular Biology, La Jolla, CA.

Abstract

A general approach for the fabrication of oriented 2-dimensional protein and virus arrays has great potential to facilitate the determination of their structure by x-ray diffraction and measurements of their surface potentials. We present here our effort towards the creation of nanoscale ordered templates with site-specific chemical linkers to proteins and viruses by two scanning probe nanolithography (SPN) techniques, dip-pen nanolithography (DPN) and nanografting. The orientations of these proteins and viruses can be controlled by introducing chemoselective functional groups on their surfaces complementary to the specific chemical linkers on the surface templates. We will present a rapid and efficient solid phase synthesis approach for the preparation of these chemoselective linkers. We will also report results of patterning viruses on templates fabricated by SPN and micro-contact printing. Preliminary results using these templates to direct the growth of virus crystals will also be discussed.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ADVANCES IN HIGH SENSITIVITY MICROCOIL NMR

Sarah C. Chinn¹, Julie L. Herberg¹, Robert S. Maxwell¹
Anthony F. Bernhardt², Vince Malba²

¹Chemical Biology & Nuclear Science Division, LLNL

²Electronics Engineering Technologies Division, LLNL

Abstract

It is well known that nuclear magnetic resonance (NMR) offers a non-destructive, powerful, structure-specific analytical method for the identification of suspect analytes. Integration of NMR methods with various separation techniques such as liquid chromatography (LC/NMR) enables detailed spectroscopic analysis of complex mixtures. An increasing need for field detection of chemical and biological agents warrants the development of a portable LC/NMR system. However, conventional NMR analysis is limited by sensitivity and resolution, resulting in the need for large sample volumes and extremely homogeneous, high magnetic fields produced by superconducting magnets. While recent advances in micro-receiver technology have demonstrated a >70-fold increase in detection limits, current portable NMR systems remain limited by magnetic field and resolution and are not compatible with other analytical techniques.

Progress towards a portable LC/NMR system involves the combination of a homebuilt NMR probe containing the microcoil with a 2 Tesla permanent magnet weighing only ~1 kg. Initial NMR results obtained with both 1 mm and 360 μm O.D. receiver coils will be presented along with ongoing methods of resolution enhancement and the future integration of an LC system. Additionally, the extension of microcoil technologies to lab-based NMR systems will be presented. Current and future applications of both portable and lab-based microcoil NMR techniques will be discussed.

This work was performed under the auspices of the U. S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48

ENHANCING MAGNETOSTRICTION BY EXCHANGE-COUPPLING IN MAGNETIC NANOPARTICLES

Wonyoung Choe¹, Harry Radousky², Mike McElfresh³
Susan Kauzlarich⁴, Kai Liu⁴, Ami Berkowitz⁴, Julian Carrey⁴

¹Materials Science and Technology Division, LLNL

²University Relations Program, LLNL

³CMS Associate Director Office, LLNL

⁴University of California Davis, Davis, CA

Abstract

Magnetostriction is an important magnetic property because the changes in the linear dimensions of a magnetostrictive material upon applied magnetic field can be used in chemical/biological sensors and actuators. One of the distinct advantages over its electronic counterpart, piezoelectricity, is its ability to be operational without contacting the power source. The interests in magnetostrictive materials with large magnetostriction at low fields are considerably increasing in recent years because of potential applications such as NEMS medical devices and chemical sensors, where remote sensing issue is critical. In order to enhance magnetostriction, we study nanosize effect on ferromagnetic Ni nanoparticles and exchange coupled core-shell nanoparticles, where Ni core is coated with other magnetic layers. Ni and core-shell nanoparticles are synthesized by solution reverse micelle technique. Here, core and shell thickness are independently controlled. The magnetic properties of Ni nanoparticles and its coated particles are compared. Preliminary work on newly developed magnetostrictive Fe-Ga alloys is also presented.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

SILICON OXIDE IN METAL OXIDE MATRICES: SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS AS ENERGETIC NANOCOMPOSITE MATERIALS

Brady J. Clapsaddle¹, Alexander E. Gash¹, Joe H. Satcher¹, and Randall L. Simpson²

¹Chemistry and Chemical Engineering Division, LLNL

²CMS Associate Director Office, LLNL

Abstract

The preparation and characterization of several unique metal oxide/silicon oxide nanocomposite materials in which the metal oxide is the major component will be presented. Traditionally, metal oxides have been prepared in silica matrices, with the composite materials typically containing < 40 wt% metal oxide. A novel sol-gel approach has proven successful in preparing silica in metal oxide matrices using common salts of Fe³⁺, Cr³⁺, Al³⁺, In³⁺, Ga³⁺, Sn⁴⁺, Hf⁴⁺, Zr⁴⁺, Nb⁵⁺, Ta⁵⁺, and W⁶⁺ and appears to be general to a large number of other metal salts, including the rare earth metals. In all cases, silica is present within a metal oxide matrix (mol ratio of metal/Si \geq 1) and silica dispersion throughout the bulk material is extremely uniform on the nanoscale. Furthermore, due to the large availability of organically functionalized silanes, the current method represents a unique way of introducing organic functionality into bulk metal oxide materials. Specifically, the synthesis and characterization of iron(III) oxide/silica nanocomposites, as well as their organically functionalized counterparts, will be discussed. These hybrid organic/inorganic nanocomposites show considerable promise in the field of nanoenergetic materials.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

A HIGH EFFICIENCY, HIGHLY SELECTIVE BIOLOGICAL AEROSOL MONITORING SYSTEM

Keith Coffee

Chemical Biology & Nuclear Science Division, LLNL

Abstract

Biological Aerosol Mass Spectrometry (BAMS) is an emerging technique being developed at Lawrence Livermore National Laboratory. The current system detects aerodynamic size and chemical composition of single particles in real time and acquires data at approximately 2 Hz. Presented here are proposed additions to BAMS that will increase efficiency and selectivity. The new system will use of several analytically orthogonal methods to detect the size, shape, biological nature, and chemical composition of individual aerosol particles at kilohertz rates. The new system will provide more accurate concentration determinations permitting the assessment of when and if dangerous levels of biological agents are encountered. The technologies that it will incorporate include virtual impaction, sonic and/or aerodynamic particle focusing, optical characterization of particle size and shape, and fluorescence and mass spectrometry to discern chemical makeup compositions. The combination of these technologies in an integrated system constitutes the most complete and versatile analytical tool to date for the characterization of aerosols of any chemical nature, in-situ and in real time.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

IMPULSIVE STIMULATED LIGHT SCATTERING UNDER EXTREME CONDITIONS

Jonathan Crowhurst

Chemistry and Chemical Engineering Division, LLNL

Abstract

A new spectrometer to perform impulsive stimulated light scattering (ISLS) measurements has recently been completed in Building 235. It has been set up primarily to measure elastic constants of metals, and speeds-of-sounds in fluids, under conditions of high pressure and temperature in the diamond anvil cell. We will briefly discuss the nature of ISLS and will show that it is complementary to other techniques such as inelastic x-ray scattering and Raman scattering. We will present results obtained from the opaque solids: germanium, tantalum, iron, and cobalt, and from the transparent fluids: formic acid, and mixtures of methanol and ethanol. Where possible, our results will be compared to theoretical predictions. We will also briefly describe separate measurements to determine the coefficient of friction and the strength properties of metals under conditions of high hydrostatic pressure. Time permitting we will discuss our Raman measurements on single-crystals of the high-T_c superconductor MgB₂, that were carried out under simultaneous conditions of high pressure and low temperature. The latter research was performed in collaboration with the Geophysical Laboratory.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ANALYSIS OF INDIVIDUAL CELLS AND ENDOSPORES BY MICRO-RAMAN SPECTROSCOPY

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James Chan², Rod Balhorn³, and Stephen M. Lane²

¹ Chemical Biology & Nuclear Science Division, LLNL

² Physics and Advanced Technologies, LLNL

³ Biology and Biotechnology Research Program, LLNL

Abstract

Micro-Raman spectroscopy is a valuable method for the nondestructive chemical analysis of biological systems. Using this technique, we have initially collected Raman spectra from individual bovine sperm cells. The high spatial resolution of this technique allows for compositional analysis of different sections of the cells. We have also collected the Raman spectra of individual bacterial endospores from four species in the genus *Bacillus*. The spectra were generally dominated by scattering from calcium dipicolinate, although scattering assignable to protein bands was also observed. A small fraction of the spores did not exhibit Raman scattering from calcium dipicolinate, possibly due to incomplete sporulation. This variability in spore composition was not discernible with ordinary light microscopy. Finally, we have begun Raman experiments on single, optically trapped spores in solution using laser tweezers. Optical trapping of the spores allows for real-time spectroscopic analysis as the solvent environment is varied. These examples demonstrate the applicability of micro-Raman spectroscopy as a non-invasive method for investigating variability in the composition of cells.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract number W-7405-Eng-48.

REAGENTLESS REAL-TIME IDENTIFICATION OF INDIVIDUAL MICRO-ORGANISMS BY BIOAEROSOL MASS SPECTROMETRY

David P. Fergenson¹, Maurice E. Pitesky², Herbert J. Tobias¹, Gregg A. Czerwieniec³, Scott C. Russell³, Carlito B. Lebrilla⁴ and Eric E. Gard¹

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²BBRP Biodefense Division, LLNL

³University Relations Program, LLNL

⁴University of California Davis, Davis, CA

Abstract

The instantaneous physical and chemical characterization of many individual airborne cells in rapid succession would be ideal for the detection of bioaerosols that have been intentionally released during a biological weapons attack. In order to provide this functionality, Bioaerosol Mass Spectrometry (BAMS) combines the power of real-time single particle laser mass spectrometry with that of real-time data analysis on each of the spectra individually. Here we present the ability of BAMS to differentiate individual airborne micro-organisms in their spore and vegetative forms on the basis of species, genus, gram stain and acid fastness in real time.

The mass spectrometer used was originally designed for environmental analysis, and so is fairly low in mass range and resolution. The mass spectra analyzed, therefore, should reflect only the fundamental chemical composition of the micro-organisms. Nonetheless, spectra from Gram negative and Gram positive bacteria exhibited obvious differences, as did spectra from acid fast versus non acid fast bacteria. In the case of the *Bacillus* spores, most of the peaks could be related to the known chemical components of the spores such as dipicolinic acid, its calcium ligand, phosphates and amino acids. Evidence of the metabolic process that produces dipicolinic acid was also observed. The identities of peaks were confirmed by the analysis of chemical standards and also spores grown on stable isotope-enriched growth media. The mass spectra from different *Bacillus* spores were extremely similar but certain peaks were unique to certain species and individual species and groups of species could, by and large, be discerned from one another at the level of a single organism. These differences between spectra from different bacillus spore species and bacterial genera are currently being exploited by an automated data processing algorithm to identify individual micro-organisms in real-time.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

POSITRON ANNIHILATION SPECTROSCOPY AND SMALL ANGLE NEUTRON SCATTERING CHARACTERIZATION OF NANOSTRUCTURAL FEATURES IN IRRADIATED Fe-Cu-Mn ALLOYS

S.C. Glade¹, B.D. Wirth², P. Asoka-Kumar³, P.A. Sterne³, and G.R. Odette⁴

¹Materials Science and Technology Division, LLNL

²University of California Berkeley, Berkeley, CA

³H Division, LLNL

⁴University of California Santa Barbara, Santa Barbara, CA

Abstract

Irradiation embrittlement in nuclear reactor pressure vessel steels results from the formation of a high number density of nanometer sized copper rich precipitates and sub-nanometer defect-solute clusters. We present results of study to characterize the size, number density, and compositions of simple binary and ternary Fe-Cu-Mn model alloys using complementary positron annihilation spectroscopy (PAS) and small angle neutron scattering (SANS). Using a recently developed spin-polarized PAS technique, we have also measured the magnetic properties of the nanometer-sized copper rich precipitates. The model alloy results show a clear effect of Mn on precipitate evolution, as alloys and steels with higher Mn (and Ni) had a larger number density of smaller precipitates. Mn also retards the precipitation kinetics and inhibits large vacancy cluster formation, suggesting a strong Mn-vacancy interaction that reduces radiation-enhanced diffusion. Finally, the spin-polarized PAS measurements reveal the non-magnetic nature of the copper precipitates, discounting the notion that the precipitates contain significant quantities of Fe, and providing an upper limit of at most a few percent Fe in the precipitates.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48 and partially supported by the U.S. Nuclear Regulatory Commission.

A THREE-DIMENSIONAL MODEL OF INTERCELLULAR SIGNALING IN EPITHELIAL CELLS

Aaron Golumbfskie

Chemical Biology & Nuclear Science Division, LLNL

Abstract

Nature has designed a highly regulated system for the transport of ions and small molecules across the epithelial barrier that separates the surfaces of the body from the external environment. These systems contain regulatory elements controlled by external and internal signals. In order to understand the complexity of these systems, we have developed a fully three-dimensional model of calcium signaling in epithelial cells. The model is based on a set of reaction diffusion equations that are solved on a large-scale finite-element code in three dimensions. We have explicitly included the major compartments in the cell (i.e. the nucleus and endoplasmic reticulum). The model allows for buffering of free Ca^{2+} , calcium induced calcium release (CICR), and for the explicit inclusion of mobile buffers, mimicking the dyes used in the experiments. Additionally, we have considered intercellular transport by including a realistic representation of the gap junctions that have a significant effect on the Ca^{2+} wave propagation. In order to make quantitative comparisons to experimental results, we have used fluorescence microscopy images of cell tissue to generate an accurate mesh. Using this realistic geometry, we will present results for the Ca^{2+} wave propagation through the tissue as a function of both initial conditions used to start the wave and various geometrical parameters that affect propagation such as gap junction density and distribution, and presence of nuclei.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

LASER-INITIATED NANOSCALE MOLECULARLY IMPRINTED POLYMERS

Brad Hart

Chemical Biology & Nuclear Science Division, LLNL

Abstract

Molecular imprinting is a process for synthesizing materials that contain highly specific recognition sites for molecules. We are investigating the synthesis of nanoscale molecularly imprinted polymers (MIPs) that will impact applications such as chemical and biological sensing and microscale separations and catalysis for use in lab-on-a-chip technologies. These materials are prepared using a focused laser to initiate polymerization on the surface of a glass substrate. Arrays of these features can be prepared on a surface with each polymer imprinted for a different molecule of interest. Thus, the response of the array may reveal a ‘fingerprint’ indicative of the molecular composition of a particular sample.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

INVESTIGATION OF Ti-DOPED NaAlH₄ BY SOLID-STATE NMR

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Abstract

In recent years, the development of Ti-doped NaAlH₄ as a hydrogen storage material has gained attention because of its dramatically improved percentage of hydrogen incorporation of approximately 5 wt. % of H₂. The addition of catalyst-precursors, such as TiCl₃, has improved the kinetics of the absorption and desorption of hydrogen from NaAlH₄. Through the analysis of X-ray diffraction studies, D. Sun et al. [1] have suggested that the Ti might be substituting into the bulk of the NaAlH₄. E.H. Majzoub et al. [2] have further concluded that the Ti-halide catalyst-precursor is independent of the valence state of the Ti-halide. However, the role that Ti³⁺ plays on enhancing the absorption and desorption of H₂ is still unknown. In the present study, ²⁷Al, ²³Na, and ¹H MAS NMR have been performed to understand the structural impact that Ti³⁺ has on the bulk NaAlH₄ material. All experiments were performed with pure NaAlH₄ and NaAlH₄ doped with Ti to fully understand how the Ti impacts this complex network. ²⁷Al--¹H and ²³Na--¹H double resonance experiments were performed to understand structural changes that occur with the addition of the Ti-precursor. Also, T₁, T₂, and multiple quantum ¹H NMR experiments were performed to gather insight into the structure and dynamics of ¹H within Ti-doped NaAlH₄.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

[1] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, C.M. Jensen, *J. Alloys Comp.* 337 (2002) L8-L11

[2] E. H. Majzoub, K.J. Gross, *J. Alloys Comp.*, 1 (2003) in press

STOCHASTIC DISLOCATION DYNAMICS SIMULATIONS OF PLASTIC DEFORMATION IN IRRADIATED METALS

Masato Hiratani

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Abstract

The nanoscale defects produced under the fusion reactor environments play a key role in determining macroscopic mechanical properties in irradiated metals. In the present work, a discrete stochastic dislocation dynamics (SDD) model is developed to investigate the effect of the irradiation defect structures on dislocation motion in nano-mesoscale. In the SDD scheme, dislocation dynamics is described as the Brownian motion of discretized dislocation segments that follows the Langevin equation of motion. The model takes into account the applied forces, images, the elastic interactive forces among the dislocations and the local defects, and stochastic forces due to collisions with phonons and electrons as constituents of Peach-Koehler forces. Due to the thermal agitation, the SDD is capable of realistic thermal processes without unphysical freeze of dislocations at the energetic local minima.

Simulation results in fcc metals with random arrays of sessile defects show jerky plastic response due to pinning and depinning of dislocations by the thermal activations and the dislocation inertial bypass. Also, the irradiation dosage is found to affect the cross slip rate, and hence, dislocation structure evolution. In the simulation of bcc metals, dislocation decoration and locking by the glissile interstitial loops are reproduced.

Moreover, our signal processing reveals spatio-temporal patterning, i.e. strain localization during relaxation, the Portevin-Le Chatelier type multi-fractal behavior or the chaotic behavior of the plastic strain according to the loading conditions. These data may be useful to check the consistency among various models spanning over different scales.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

NANOMECHANICAL BEHAVIOUR OF MULTI-COMPONENT METASTABLE MATERIALS

A.M. Hodge and T.G. Nieh

Materials Science and Technology Division, LLNL

Abstract

Intensive efforts have been carried out over the past decade to develop means to slow down the phase transformation kinetics during the synthesis of multi-component metastable materials. As a result of these efforts, some metallic glasses can now be fabricated from the liquid state at cooling rates of about 1–10 K/s, which are close to those of conventional casting. This enables the production of metallic glasses with a thickness over 10 mm. Bulk amorphous alloys have many potential applications resulting from their unique properties, such as superior strength and hardness, excellent corrosion resistance, shaping and forming in a viscous state, reduced sliding friction and improved wear resistance, and low magnetic energy loss. Instrumented nanoindentation techniques are effective to study the nanomechanical properties of metallic glasses. A nanoindenter is a novel instrument that can be used to explore the properties of materials, such as thin films, multilayers, and soft tissues, with an extremely small volume (~nm). These properties are extremely useful for the understanding and modeling of materials on a nanometer scale. For example, the compressive stress immediately under a nanoindenter is extremely high; it can be as high as 200 kbar. Materials are expected to exhibit unusual response under this extreme condition.

In this presentation, we demonstrate the successful application of instrumented nanoindentation techniques for characterizing deformation behavior of multi-component metastable materials, in particular, metallic glasses. The hardness and elastic modulus of several metallic glasses were investigated using a nanoindentation technique. Abrasive wear properties of these metallic glasses were also evaluated using nanoscratch techniques under a ramping load, and a direct comparison of their wear resistance was made. Damage on scratched surfaces was examined using SEM and AFM. The scratched surface was observed to be significantly different for materials with different compositions. A modified Archard equation was proposed to model the ramping load test. It was found that the wear resistance of metallic glasses is not necessarily proportional to the nanohardness of the materials, as described by the classical Archard equation. This discrepancy was suggested to be a result of different wear mechanisms operating in various materials.

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SUPPRESSION OF A PREMIXED C₃H₈-AIR FLAME BY HALOGENATED AND PHOSPHORUS-CONTAINING COMPOUNDS

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²CMS Associate Director Office, LLNL

Abstract

Calculations were performed using the HCT (Hydrodynamics, Chemistry and Transport) code to investigate the means by which different suppressants act on a premixed, propane/air flame. Two classes of suppressants are investigated: halogenated, HBr, CF₃Br, and phosphorus-containing compounds, dimethyl-methylphosphonate (DMMP) and sarin (POFCH₃OC₃H₇). Although investigations of these compounds has been performed by various authors, no known previous work has been performed to directly compare the suppression mechanism between the halogenated compounds (HBr and CF₃Br) and phosphorus-containing compounds, or PCCs (DMMP and sarin) in a premixed flame. Of particular interest is a comparison of the location in the flame that the suppressants act. It has been shown that for phosphorus-containing compounds, radical recombination reactions reduce radical concentrations near the post-flame region, as opposed to the halons, which primarily exhibit recombination in the pre-flame zone. This behavior leads to the greater effectiveness of the organophosphorus suppressant compared to the halogenated suppressants.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ION-IRRADIATION-PRODUCED DISORDERING IN WIDE BAND-GAP SEMICONDUCTORS

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Abstract

Recently, there has been much interest in wide band-gap wurtzite semiconductors such as group-III nitrides (GaN, AlGaN, and InGaN) and ZnO. Such interest has been stimulated by important technological applications of these materials in optoelectronics as well as in high-temperature/high-power and radiation-resistant electronics. In the fabrication of ZnO-based and group-III-nitride-based devices, ion bombardment represents a rather attractive processing tool for selective-area doping, electrical and optical isolation, and etching. However, ion-beam-produced lattice disorder and its undesirable consequences limit technological applications of ion implantation.

In this presentation, I focus on some of our recent results showing that ion-beam-defect processes are considerably more complex in these wurtzite semiconductors than in the case of both elemental and group-III-V cubic semiconductors. In particular, I discuss a range of rather unusual effects in the damage buildup behavior in GaN. I also present an unusual damaging behavior in ZnO with the formation of a middle defect peak; i.e., a defect peak between the expected surface and bulk peaks of disorder. Finally, I discuss how aluminum and indium content can dramatically influence the damage buildup behavior in AlGaN and InGaN ternary alloys. We find that an increase in In concentration strongly suppresses dynamic annealing processes (i.e., defect migration and interaction processes) and, hence, enhances the buildup of stable lattice disorder in InGaN under ion bombardment. In contrast, an increase in Al content dramatically increases dynamic annealing in AlGaN. Throughout the presentation, emphasis is given to understanding physical mechanisms responsible for such an extreme damaging behavior, the susceptibility of these semiconductors to ion-beam disordering, and to the crystalline-to-amorphous phase transition.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

STRUCTURES AND DYNAMICS OF AIR-WATER INTERFACE FROM *ab initio* MOLECULAR DYNAMICS

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Abstract

Stable air/water interface calculations were performed using *ab initio* molecular dynamics simulations based on the Car-Parrinello approach. The air/water interface is of interest because of its importance in many areas of scientific interest, such as atmospheric chemistry, as well as being a medium where many experiments are conducted in biological science. To model the air/water interface, a slab of water approximately 35Å in depth was simulated using a 2-D periodic boundary condition on the pico-second timescale using *ab initio* molecular dynamics simulations. From these simulations, we were able to determine the structure, dynamics, and electronic properties of water near the air/water interface from first principles.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ANISOTROPY REVEALED IN A MAGNETIC FIELD: A STUDY OF SINGLE CRYSTAL $\text{Ca}_3\text{Ru}_2\text{O}_7$

Scott McCall

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Abstract

The Ruddlesden Popper (RP) series of ruthenates, of the general form: $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ are a series of perovskite-like layered compounds with n layers of RuO_6 octahedra separated by a rock salt layer. Collectively, this series displays a wide variety of interesting physical properties including superconductivity, metal-insulator transitions, itinerant ferromagnetism, and metamagnetism. $\text{Ca}_3\text{Ru}_2\text{O}_7$, the two layered flavor, is orthorhombic with lattice constants $a=5.3720(6)\text{\AA}$, $b=5.5305(6)\text{\AA}$, and $c=19.572(2)\text{\AA}$, where the difference between the two in-plane values arises from the tilting between RuO_6 octahedra in neighboring planes. In the absence of an external magnetic field, the system is a metallic paramagnet which orders antiferromagnetically at $T_N = 56$ K and then undergoes a spin reorientation coincident with a metal-nonmetal transition at $T_M = 48$ K, entering a metamagnetic state. When a magnetic field is applied along each of the two in-plane axes, very distinct behavior is observed for magnetization, resistivity, and specific heat measurements, leading to the construction of two vastly different HT phase diagrams. These results demonstrate that the Ru-O-Ru bond angle is critical in determining the magnetic behavior of this system, which may have implications with respect to tuning properties of the other members in this series of ruthenates.

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A 4π CAMERA FOR GAMMA-RAYS

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Abstract

This work is pursuing a new compact gamma-ray imager of high efficiency and spectroscopic resolution with a 4π field-of-view by using Compton camera concepts. One of the main advantages of such a gamma-ray imager over today's state-of-the-art Anger cameras and coded apertures will consist in its much improved sensitivity. Since this type of imager doesn't require collimators, its quantum efficiency will be 3 to 4 orders of magnitude higher. In order to insure optimal use of the photons detected in a position sensitive gamma-ray detector, new analysis methods have been developed, able to provide the accurate positions and energies for multiple gamma-ray interactions. This is ultimately important for an improved image resolution. The effective imaging capability of the position sensitive detection system is brought in by the use of new analysis methods for reconstructing the scattering sequence of the gamma-ray photon (gamma-ray tracking), and for image reconstruction using Compton camera type of data. First 4π images have been measured using a single planar Ge detector with orthogonal strips. The system we are developing will be tested in various applications, ranging from nuclear medicine, nuclear non-proliferation and environmental monitoring, to gamma-ray astrophysics.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ON THE MAGNETIC PROPERTIES OF ULTRA THIN EPITAXIAL Fe FILMS ON GaAs(001)

Simon Morton

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Abstract

The magnetic properties of epitaxial Fe films on GaAs have attracted considerable interest in recent years because of their potential for use as spin injection sources for spintronic devices; however, previous studies have been unable to demonstrate a magnetic signature in films with thicknesses below approximately 5 ML. A number of possible explanations for this observation have been proposed such as the presence of a magnetically dead interfacial layer of Fe₂As. However, by measuring the thickness and temperature dependence of the Fe 3p core level magnetic linear dichroism signal, we have shown that such films are indeed ferromagnetic but that their Curie temperature is substantially below room temperature. For instance, a T_c of approximately 240K was measured for thin films with a nominal thickness of 0.9 nm. Furthermore, the values of the Curie temperature in this thickness regime have been shown to be extremely sensitive both to initial substrate conditions and to the overall film thickness; an increase in the thickness of 0.35nm results in a Curie temperature above room temperature. These measurements have been complemented with spin resolved and angle resolved measurements of the Fe/GaAs valence band and core levels; together with ex-situ XRD and SPM studies of sample growth. The origins of the evolving magnetic behavior of Fe films on GaAs(001) from 1-50ML is discussed in terms of the spin-dependent electronic band structure and the stoichiometry and growth morphology.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ELECTRONIC STRUCTURE AND SURFACE PHYSICS OF QUANTUM DOTS

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Abstract

An important field of research recently in nanoscience is to examine the effect of an impurity atom on the physics of quantum dots (QDs). An intriguing question to ask is how an unintentional dopant, such as a surface atom, can affect the electronic, optical, and vibrational properties of the QD. Traditional analysis techniques of QDs, such as optical spectroscopy of the band gap transitions in semiconductors, provide useful, but lack surface and element specific information about the electronic structure. We have performed positron annihilation (PAS) and resonance Raman (RRS) spectroscopic measurements to understand the electronic and surface structure of colloidal CdSe quantum dots. In CdSe QDs, we have found that a size dependent electron-phonon interaction, as probed by RRS, can induce various levels of surface strain on the QDs. PAS has shown a R^{-2} scaling law for the smearing of the band gap with the high momentum annihilation spectra dictated by the surface termination of the QD. Correlation of these experiments indicates that the surface physics of QDs are very complex and cannot be ignored.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

DETERMINATION OF IODINE SPECIATION IN ENVIRONMENTAL SAMPLES USING X-RAY ABSORPTION SPECTROSCOPY

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Abstract

The study of accumulation and transport of iodine in the environment is important for the development of detection schemes for nuclear fuel reprocessing activities, whose waste streams contain the fission product ¹²⁹I. The chemical forms of iodine in the environment are numerous, and the specific chemical form is an important factor in iodine transport and accumulation in soils and biota. X-ray absorption spectroscopy (XAS) is an element-specific technique that can sensitively determine the local chemical environment of iodine in some natural samples. XAS spectra measure the oxidation state and local bonding geometry of the iodine, and can quantify the number and species of iodine neighbors as well as the iodine-neighbor bond lengths. First, we measured XAS spectra for a range of iodine-containing standard chemicals and minerals to provide a basis data set. The corresponding XAS spectra can be gathered into several groups, including inorganic, organic chain, and organic ring molecules, and mineral structures. Next, we measured iodine XAS spectra for a number of environmental samples, including iodine-containing marine samples as well as iodine sorbed upon a number of minerals. The results shed light on the nature of the carbon-iodine bond, which determines the residence time for organo-iodine compounds during biogeochemical cycling. Results from sorption studies can be used to model inorganic fate and transport.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

STANDARD RATE-THEORY PREDICTIONS OF IRRADIATION DAMAGE EVOLUTION IN COMPARISON WITH MICROSTRUCTURAL DATA

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Abstract

Structural materials in fission reactors are exposed to high-energy neutron fluencies. Predictive models will be needed for void swelling, irradiation creep and change in mechanical properties. For long-term predictions of the microstructural evolution up to tens of dpa, simple rate-theory approaches have been employed. These involve only three reactions, namely recombination of point defects, diffusion and migration of point defects to sinks, and thermal emission of vacancies from sinks. Recently however, atomistic simulations have shown that a multitude of other mobile defect clusters are generated in a large collision cascade. In particular, SIA loops are directly formed and are highly mobile.

This raises the question whether a simple rate-theory is adequate to predict microstructural evolutions under cascade damage. We test the standard rate-theory by using measured microstructural data for dislocation loops, network dislocations, and for voids as obtained from pure austenitic alloys irradiated in FFTF / MOTA.

The unknown parameters in the standard rate theory are the recombination volume, migration energies of point defects, sink bias factors and cascade efficiency. For each of these, we consider a range of possible values, and predict with the experimental sink strengths, the swelling rate. It is found that the simple standard rate-theory gives a satisfactory prediction of the observed swelling rate with parameters well within the range of acceptable values.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

THE SEARCH FOR SUPERHEAVY ELEMENTS: THE DISCOVERIES OF ELEMENTS 114 AND 116 AND INITIAL RESULTS FOR ELEMENT 118

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Abstract

One of the outcomes of nuclear structure theory and the shell model is the possible existence of an “Island of Stability”. This Island of Stability resides beyond the heaviest known stable isotopes of lead and bismuth, beyond the long-lived isotopes of uranium and plutonium. The only possible way of observing these superheavy elements is through their production using heavy ion beams and stable/long-lived isotope targets. Various theoretical calculations have been performed over the past 35 years that show the “Island of Stability” resides somewhere near Element 114, near the predicted closed shells $Z = 114$ and $N = 184$. This “Island of Stability” has been reached using ^{48}Ca ion beams and highly enriched plutonium, curium and californium targets. Latest results will be presented.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

RANDOM PROBABILITY ANALYSIS OF THE $^{48}\text{Ca} + ^{249}\text{Cf}$ EXPERIMENT

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Abstract

A long experimental run was performed at the Dubna U400 Cyclotron Facility bombarding ^{249}Cf with ^{48}Ca aimed at producing isotopes of element 118. Recent independent data analysis of the information gathered during this experiment was performed at LLNL and shall be presented. Two interesting events shall be discussed in detail. The Monte Carlo random probability analysis developed at LLNL for such heavy element experiments was performed for these data and the implications from such analysis will be presented.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

MOLECULAR MECHANISMS OF KIDNEY STONE INHIBITION BY PROTEINS AND SMALL MOLECULES

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Abstract

Understanding molecular mechanisms of biological control over calcium oxalate crystallization is crucial for development of effective stone disease therapies. Moreover, extension to other systems may suggest strategies for synthesis of biologically inspired materials. Calcium oxalate monohydrate (COM), which plays a functional role in plant physiology, is a source of pathogenesis in humans, causing kidney and renal stone disease. Despite extensive research on COM modification by proteins and small molecules, the control mechanisms remain unknown. In addition, because proteins directing COM inhibition have been identified and sequenced, it provides a realistic system for general physiochemical investigations of biomineralization. In this presentation, I will show the first molecular-scale picture of COM modulation by both osteopontin — a naturally occurring protein— and citrate — a commonly used therapeutic agent. Combining force microscopy with molecular modeling, we show that they control crystal habit and growth kinetics through anisotropic step pinning due to step-specific interactions, with both size and structure dictating their effectiveness. This work demonstrates the power of applying sophisticated physical tools to biomedical studies and lays the foundation for understanding the occurrence and treatment of stone disease.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

DOUBLE-TETHERED FORCE SPECTROSCOPY OF THE CONCAVALIN-A MANNOSE BOND

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Abstract

Many biological recognition interactions, e.g. between a bacterial toxin and a cell, involve ligands and receptors that are tethered rather than rigidly bound on cell surfaces. We have used Atomic Force Spectroscopy to directly measure the bond rupture force between a single protein and its ligand both attached to 20 nm long polymer tethers. Besides replicating a biologically relevant system, the tethers allow us to differentiate specific protein-ligand bond formation from non-specific adsorption of the protein to the support. Non-specific binding is the single most important factor that makes low-level detection of bio-agents undetectable to most devices. In addition, the ability to measure single molecule interactions allows us to determine useful physical parameters of the system, such as the range over which a tethered molecule can interact. These measurements can then be used to parameterize computer models, which in turn can be utilized in the construction of highly sensitive and efficient biodetectors.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

ALOOF TRANSMISSION ELECTRON ENERGY-LOSS SPECTROSCOPY AND ITS APPLICATION TO NANOSTRUCTURES

Bryan Reed

Materials Science and Technology Division, LLNL

Abstract

The technique of aloof electron energy-loss spectroscopy (EELS), in which the electron beam does not penetrate the material, has long been a powerful yet underutilized tool for investigating surface electromagnetic properties. The combination of two current trends suggests that it is time to bring this technique into the mainstream. These are (1) the great level of interest in nanotubes, nanowires, and quantum dots, particularly for their electronic and optical properties, and (2) the arrival of a new generation of transmission electron microscopes (TEMs), with aberration correction and monochromated electron sources. One could say there are new problems looking for analysis tools, and new analysis tools looking for problems to solve. Aloof EELS is uniquely well suited to bringing these two together.

Aloof EELS takes advantage of signal enhancement at high-curvature surfaces, vastly reduced radiation damage, and unusually clean, clear, easily-interpreted spectra. The result is a nanometer-scale characterization of valence electron behavior that is not subject to the same difficulties that plague other characterization techniques. We will discuss how various scaling laws make these advantages more and more compelling as the size of the material is reduced, drawing on our previous work with silicon tips and isolated carbon nanotubes to illustrate our points. These advantages will only get stronger with the new generation of TEMs coming online, enabling high-resolution infrared-to-deep-UV characterization of isolated nanostructures of all kinds.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. Research was performed under NSF grant number DMR9978835 at the University of Washington, Department of Materials Science and Engineering, Seattle, WA.

MODELING *Yersinia pestis* SYSTEMS BIOLOGY

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Abstract

Recent technological advances in high-throughput data collection, such as DNA microarrays and mass spectrometry profiles of protein and metabolite expression, can be used to study complex systems of infection and host immune response. These techniques typically yield noisy low-resolution measurements. Consequently, new modeling approaches are needed to help design experiments, identify and analyze potential biomarkers, and develop new therapies. Current models of biological systems either fail to include necessary biological details (e.g. Boolean logic) or require large numbers of parameters that are very difficult to accurately measure (e.g. chemical kinetics). We use fuzzy logic and finite state rule-based models to incorporate details of molecular mechanism obtained from microarray and similar experiments into higher-level models of pathogen regulation and host-pathogen interaction. We are modeling *Yersinia pestis* (plague bacteria) virulence and host interaction pathways, based on genomic, proteomic, and metabolite expression data we are collecting in our lab and with collaborators. We have fit scalable fuzzy logic and finite state models to *Y. pestis* whole genome microarray data on changes to glycolysis pathway gene expression. The model shows gene regulation that occurs under changes in temperature and calcium similar to host conditions. Initially, we have used exhaustive search to fit the model; we are exploring more efficient algorithms. Currently, we are using the data to model other *Y. pestis* pathways, using homology to *E. coli* pathways in the KEGG database as a template. Preliminary results from this work will be presented.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

DETERMINATION OF THE METABOLIC AND PHYSIOCHEMICAL STATE OF INDIVIDUAL BACTERIAL CELLS

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Abstract

A technique capable of rapidly characterizing individual microorganisms without the use of reagents is of interest in bio-defense, environmental health, aerobiology, medicine, and biomedical research. In our laboratory, we are engaged in the development of an instantaneous, reagentless, single-particle analysis technique based on Aerosol Time-of-Flight Mass Spectrometry (ATOFMS), called Bio-Aerosol Mass Spectrometry (BAMS) for the efficient screening and identification of bio-aerosols and micro-organisms of public health concern. In this work, we specifically investigate spore forming bacteria in multiple stages of their sporulation cell cycle in order to demonstrate the potential of BAMS as a tool for the determination of the metabolic and physiochemical state of individual cells. An advanced form of this capability would be potentially useful for medical diagnostics such as the sensitive identification of transformed or lytically affected cells in large populations of normal ones.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

STRUCTURAL DETERMINATION OF MYELIN OLIGODENDROCYTE GLYCOPROTEIN USING NUCLEAR MAGNETIC RESONANCE METHODS

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Abstract

Myelin oligodendrocyte glycoprotein (MOG) is an integral membrane protein of central nervous system (CNS) myelin implicated as an autoantigen in multiple sclerosis (MS). Knowledge about MOG structure, function and interactions with antibodies is crucial for elucidating its role in MS and for enabling the rational design of effective drugs to treat this disease. Yet to date, the conformation of MOG in association with the myelin membrane, as well as the exact nature of the interactions between this protein and disease-inducing immune responses, have not been determined.

We present herein progress towards solving the three-dimensional structure of MOG. Both solution- and solid-state nuclear magnetic resonance (NMR) methods were applied for structural determination. A homology model of the extra cellular domain (residues 2-120) of human MOG was constructed to map the regions that are potentially accessible to antibody binding. Circular dichroism techniques were also used to monitor effects of micro-environments on conformational changes of this protein.

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THE PROPERTIES OF ACTINIDE NANOSTRUCTURES

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Abstract

Predicting the aging behaviors of actinide materials is a problem requiring advances in both theoretical understanding and experimental observation. This work seeks to determine the various correlation and spin contributions to the electronic structure active in actinide elements through observations of structural and electronic evolution in these materials as a function of particle size. Results from these experiments will be used to confirm the several proposed theoretical descriptions of these materials. The measurements [which will include x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunnel microscopy (STM)] will be carried out on a number of different uranium and plutonium systems, such as single crystalline nanoparticles and 1-D wires, produced via pulsed laser deposition (PLD). The construction of the facility for the *in situ* growth of the nanoparticles and the suite of analytical instrumentation is nearly completed. Pulsed laser deposition of uranium on a silicon substrate has been demonstrated with the current system. The presence of deposited uranium was confirmed by XPS (MgK α) measurements in which the 4f uranium levels were observed. *Ex situ* optical microscopy and AFM measurements indicate that the uranium nanoclusters have sizes ranging from ~ 50 nm to ~ 5 μ m. Further work on uranium, including further characterization of the PLD process, will be completed before the introduction of plutonium samples into the system.

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STRUCTURE, ENERGY AND MOBILITY OF SELF-INTERSTITIAL DISLOCATION LOOPS IN VANADIUM

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Abstract

Isolated self-interstitial atoms (SIA) and SIA clusters that are produced in displacement cascades have significant impact on the microstructural evolution under neutron and high-energy charged particle beam irradiations. In the present study, we use molecular-statics and molecular-dynamics (MD) simulations based on a new Finnis-Sinclair potential to model the energy and mobility of SIA clusters in vanadium. The results are compared to experimental observations and recent results in Ferritic alloys which detail the formation mechanism responsible for the nucleation and growth mechanism of $\langle 100 \rangle$ dislocation loops. In particular, we provide an explanation for the fact that $\langle 100 \rangle$ loops are not observed in Vanadium. The SIA clusters are composed of $\langle 111 \rangle$ split dumbbells and crowdions. The clusters can be described as perfect prismatic dislocation loops with Burgers vector $b = (a/2) \langle 111 \rangle$. As the loops grow, SIAs fill successive jogged edge rows with minimum free energy cusps found at the 'magic' numbers corresponding to un-jogged filled hexagonal shells. The total energy of the clusters is in excellent agreement with continuum elasticity dislocation theory predictions. The SIA clusters are highly mobile and undergo one-dimensional motion along their glide prism. The high cluster mobility is related to the easy motion of kinked dislocation loop segments, which propagate along the loop periphery resulting in increments of prismatic glide. Linking atomistic point defect cluster calculations, dislocation theory and experimental results provide a powerful tool in understanding radiation damage.

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EFFECTS OF GRAIN BOUNDARY CONSTRAINT ON THE CONSTITUTIVE RESPONSE OF TANTALUM BICRYSTALS

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Abstract

The role of grain boundary constraint in strain localization, slip system activation, slip transmission, and the concomitant constitutive response was examined performing a series of uniaxial compression tests on tantalum bicrystals. Tantalum single crystals were diffusion bonded to form a (011) twist boundary and compressed along the [011] direction. The resulting three-dimensional deformation was analyzed via volume reconstruction. With this technique, both the effective states of stress and strain over the cross-sectional area could be measured as a function of distance from the twist boundary, revealing a highly constrained grain boundary region. Post-test metallurgical characterization was performed using Electron Back-Scattered-Diffraction (EBSD) maps. The results, a spatial distribution of slip patterning and mapping of crystal rotation around the twist-boundary, were analyzed and compared to the known behavior of the individual single crystals. A rather large area near the grain boundary revealed no crystal rotation. Instead, patterns of alternating crystal rotation similar to single crystal experiments were found to be some distance away (~1mm) from the immediate grain boundary region, indicating the large length scale of the rotation free region.

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