SYMPOSIUM Q

Neutron and X-Ray Scattering as Probes of Multiscale Phenomena

November 29 - December 1, 2004

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* Invited paper
SESSION Q1: X-rays and Neutrons as Probes of Local Atomic Order
Chair: Peter Khalifah
Monday Morning, November 29, 2004
Hampton (Sheraton)

8:30 AM Q1.1
Application of High Energy X-rays to Quantitative Measurements of Reciprocal Space: Superstructure and Charge Ordering in Nd1BaCoO4.
Peter Chupas1, Stephan Rosenkranz1, Raymond Osborn2, John F. Mitchell1 and Peter L. Lee2
1Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 2Experimental Facilities Division, Argonne National Laboratory, Argonne, Illinois.

Many new phenomena of considerable technological importance are driven or strongly enhanced by disorder and the nanoscale self-organization associated with it. A powerful probe of such defect structures, including possible defect-defect correlations, superstructures, twinned crystals, and charge/orbitally disordered self-organization associated with it, is provided by single crystal diffuse scattering. A detailed understanding of complex disorder however requires the measurement of both Bragg and diffuse scattering over large volumes of reciprocal space as well as efficient analytical tools for analyzing and modeling this data. Utilization of the rotation method coupled with area detectors allows the collection of high quality data on such systems, efficiently and surveyed for subtle scattering features, but there are numerous difficulties which have prevented wide spread use of this technique. Diffuse scattering extends broadly throughout Q space and is commonly a several orders of magnitude weaker than Bragg scattering, which makes stringent demands when making quantitative measurements of both Bragg and diffuse intensities. The application of high energy X-rays is crucial for to make meaningful measurements of both Bragg and diffuse intensities, which would otherwise rely on variables such as sample shape, and further, allows high values of the scattering vector, Q, to be probed, which are necessary to accurately decipher the magnitude of small deviations from the average structure. We present results of measurements we have made at beamline 1-ID at the Advanced Photon Source, testing the quality of quantitative measurements made using the rotation method approach and illustrating the application of the method to the study of the superstructure and charge ordering in Nd1BaCoO4.

8:45 AM Q1.2
Temperature Dependent Dynamic Pair Correlations in Relaxor Ferroelectric from Inelastic Neutron Scattering.
Wojciech Dmowski1, Takeshi Egami2,1, I. K. Jeong3, R. H. Heffner3, J. S. Park1, K. H. Song4, M. Hohen5 and F. Trouw5
1Univ. Tennessee, Oak Ridge Nat. Lab., Knoxville, Oak Ridge, Tennessee; 2Univ. of Delaware, Newark, Delaware; 3Los Alamos Nat. Lab., Los Alamos, New Mexico; 4Univ., Seoul, South Korea; 5LANSCE, Los Alamos Nat. Lab., Los Alamos, New Mexico.

Relaxor ferroelectric oxides, such as Pb(Mg1/3Nb2/3)O3 (PMN), show a diffuse maximum of dielectric susceptibility at the freezing temperature.Susceptibility peak is frequency dependent with a broad relaxation spectrum. We have described the presence of local polar domains above formal Tc, as evidenced by optical and dynamic pair correlation functions. The dynamic correlation can be obtained from the conventional X-ray structure factor by performing Fourier transformation for several energy slices to obtain dynamic pair correlation functions. The dynamic correlation can be compared to the static one, which is obtained from the regular synchrotron or the neutron diffraction data. The main advantage of inelastic neutron scattering is the possibility to study the collective motion between tetrahedra. The main advantage of inelastic neutron scattering is the possibility to study the collective motion between tetrahedra. In this talk, I will discuss recent resonant diffusion measurements at the Mn L-edges, which allows one to study the magnetic, orbital and spin correlations in the near-half doped manganite Pr0.6Co0.3. Comparison the widths of the magnetic, Q = (1/2,0,0), and orbital, Q = (0,1,2,0), diffraction peaks we found that the magnetic scattering length exceeded that of the orbital by nearly a factor of two. Furthermore, we observed a large (3 eV) spectral weight shift between the magnetic and orbital resonant line shapes. The discrepancy between the orbital and magnetic correlation lengths is difficult to explain if the orbital order determines the magnetic exchange pathways. In addition, the spectral weight shift appears at around the conventional CEF picture in which Mn3+ and Mn4+ sites contribute to the magnetic (1/2,0,0) and orbital (0,1/2,0) scattering. In order to calculate the magnetic and orbital resonant line shapes, we have described the ground state in terms of a “relaxed” charge order model.

9:00 AM Q1.3
Revisiting the ground state of an insulating, half-doped manganite using x-ray resonant scattering.
Jessica Thomas1, John Hill2, Stephanie Grenier1, Peter Abbamont2, and Michel van Veenendaal2,3.
1Argonne National Laboratory, Upton, New York; 2Northern Illinois University, Dekalb, Illinois; 3Amsterdam Netherland.

X-ray and neutron diffraction experiments support a picture of charge ordering in the Mn sites in a number of half-doped, insulating manganites. In this picture, proposed by Goodenough to explain the complex "CE" type magnetic ground state, distinct sub-lattices of Mn3+ and Mn4+ sites form at Tc. The Mn3+ sites are John-Teller active and a cooperative lattice distortion and orbital ordering of the Mn3+-sites occurs at the same temperature as the charge ordering. Magnetic ordering occurs either coincident with, or below, the charge-oralbit order transition temperature. However, the dynamics which lead to this particular ordering are still not understood. For example, it is unclear whether it is the magnetic interactions which stabilize the orbital and charge order or the charge and orbital order is simply a precursor to the magnetic ground state. Furthermore, the degree to which the charge separation into Mn3+ and Mn4+ sites complete remains a controversial issue. Resonant X-ray scattering near the atomic Mn L-III absorption edges (2p -> 3d) is a powerful probe for studying orbital and spin correlations in manganites. At the Mn L-edges (~550 eV), the scattering amplitude is directly sensitive to the anisotropies in the 3d electronic environment which result from orbital ordering while the resonant enhancement of the magnetic scattering is enormous. In addition, the energy dependence of the resonant line shape yields a detailed spectroscopy of the unoccupied 3d states in the ordered phase. Combined with theoretical calculations, a measurement of the resonant line shape provides an important test of the ground state in these materials. In this talk, I will discuss recent resonant diffusion measurements at the Mn L-edges which allowed a direct comparison of orbital and spin correlations in the near-half doped manganite Pr0.6Co0.3. Comparison the widths of the magnetic, Q = (1/2,0,0), and orbital, Q = (0,1,2,0), diffraction peaks we found that the magnetic scattering length exceeded that of the orbital by nearly a factor of two. Furthermore, we observed a large (3 eV) spectral weight shift between the magnetic and orbital resonant line shapes. The discrepancy between the orbital and magnetic correlation lengths is difficult to explain if the orbital order determines the magnetic exchange pathways. In addition, the spectral weight shift appears at around the conventional CEF picture in which Mn3+ and Mn4+ sites contribute to the magnetic (1/2,0,0) and orbital (0,1/2,0) scattering. In order to calculate the magnetic and orbital resonant line shapes, we have described the ground state in terms of a “relaxed” charge order model.

9:30 AM Q1.4
Pair Distribution Function as a Probe for Zeolite Structures.
Maria Martinez-Inesta1, Inmaculada Peral1, Thomas Profeta2 and Raul Lobo1
1Univ. of Delaware, Newark, Delaware; 2NIST Center for Neutron Research, College Park, Maryland; 3Los Alamos Neutron Science Center, Los Alamos, New Mexico.

Zeolites are often cited as examples of perfect crystals with ideal periodic long-range order. In practice, however, disorder is introduced in many forms. The way this is usually dealt with, using standard crystallography methods, is by the development of models that describe the distortions caused by disorder in an average way. At the atomic level methods such as solid state NMR and optical spectroscopies are used to gain knowledge about the local chemical environments and geometry surrounding selected atoms in a sample. However, these approaches do not help solve many of the problems associated with understanding diffusion and the catalytic and adsorptive properties of zeolites, mainly because the need for precise atomic models to understand these problems. The objective of my research is to adapt the a technique called Pair-Distribution Function (PDF) to the study of local structure in zeolites in order to fill the gap in information that currently exists for the understanding of zeolite physical and chemical processes. A first study is dedicated to understanding the structure of disordered zeolite beta, a zeolite that is sometimes used in refineries as additive to fluid catalytic cracking processes to optimize yield. The structure of zeolite beta is described as an intergrowth of two hypothetical polytypes A and B. Both of this polytypes have an identical lattice of pores that is stacked differently in the c direction. This layer is extended infinitely in a b and has a height of approximately 7 A along the c direction. Thus, the structure of these polytypes were refined using neutron and synchrotron data up to 7 A. Refinements using only the synchrotron or the neutron datasets gave results inconsistent with each other but a cyclic refinement of the two datasets gave a good fit to both PDFs. The refinement show that the PDF method is a viable method to analyze the local structure of disordered zeolites. A second study is a work in progress geared toward the determination of the mechanism of the negative thermal expansion of zeolite chabazite, which has been found to be one of the mostcontracting materials known. Using the synchrotron PDF at room temperature and at 75K. Preliminary results show that the structures of the tetrahedra are unchanged with temperature suggesting that the mechanism is likely to be some motion between tetrahedra.
Typical metallic glasses are obtained by rapid quenching from a melt with cooling rates on the order of 10^5-10^6 K/s. Below the glass transition temperature, viscosity increases by several orders of magnitude and the supercooled liquid forms a glass. The resultant glass is metastable: it can transform to the same glassy solid but also can undergo subtle structural changes if annealed at low temperatures. The latter effect is called structural relaxation.

Structural relaxation can affect elastic, magnetic, diffusivity, electrochemical and other properties and can be directly observed through structural studies using neutron, X-ray, or electron scattering. Bulk-metallic glasses (BMGs) are special compositions of metallic glasses that can form massive (bulk) glasses alloys with very low cooling rates (~ 1 K/s). Since the cooling rate is so low, one would expect that the low-temperature annealing would have a small effect on the structure. Surprisingly, we can observe pronounced changes in the local atomic structure as described by the pair distribution function (PDF). A BMG alloy with a nominal composition of Zr52.5Cu17.6Ni14.6Al10.0 (at.%), commonly known as Vitreloy 105 (Vit 105), was prepared by arc-melting and drop-casting in a water-cooled copper mold under a Zr-gettered, Ar atmosphere at the Oak Ridge National Laboratory. Isothermal annealing was performed in vacuum, below T_g, at 630 K for 0 (as-cast), 10, 20, 30, 40, and 60 minutes to obtain samples with various states of structural relaxation. Structural studies were performed using time-of-flight neutron diffraction, high energy X-ray diffraction and small-angle scattering. Differential scanning calorimetry was used to examine changes in the specific heat, which were correlated to the amount of structural relaxation in the various samples. Neutron-scattering studies were conducted on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS), and X-ray studies were conducted at the Advanced Photon Source (APS) and National Synchrotron Light Source II (NSLS II) beamlines. All of the resultant spectra demonstrated broad, amorphous peaks without any sharp, crystalline peaks. PDF analysis was conducted to examine the change in the bond length distribution as a function of annealing time. It was found that the nearest-neighbor bond length distribution narrowed with increasing annealing time, indicating that atoms relax such that extreme (long and short) bonds are eliminated.

Acknowledgements

This work was supported by the National Science Foundation Integrative Graduate Education and Research Training (IGERT) Program in Materials Lifetime Science and Engineering, managed by Drs. L. Clesceri, W. Jennings, and L. Goldberg; and the International Materials Institutes (IMI) Program, under DMR-0231320, Dr. C. Huber.

10:30 AM *Q1.6

Direct Observation of Charge Order in La0.5Sr2RuO4
L. Hao1, F. D. Meier2, S. Schuessler-Langehem1, T. Justus1, S. Schlapbach1, Zhihe Hu1, Maurits W. Hoverkort1, Mohammed Benomar1, Oliver Fried1, Markus Braden2, Arata Tanaka2, Enrico Schierle3, Holger Ott1, Eugen Weschke4, Guenter Kaindl4, George A. Sawatzky5, II. Physikalisches Institut, Universitaet zu Koeln, Koeln, Germany; 2National Research Council, Canada; 3NSLS, Brookhaven National Laboratory, Upton, New York

We report about the direct observation of charge order in Sr-doped La_{2/3}Sr_{2}RuO_{4} using resonant soft-x-ray diffraction at the Ni L_2,3 edge. Neutron-scattering studies and La M_4,5 resonances. Unlike conventional diffraction techniques, which are essentially probing lattice modulations, resonant soft x-ray diffraction is very sensitive to the oxidation state and hence particularly suited to study charge-order phenomena. The charge-order superstructure peak from La_{2/3}Sr_{2}RuO_{4} shows a resonant enhancement predominantly at Ni L_{2,3} edges, in contrast to the x-ray absorption signal, which is dominated by the La absorption. The details of this energy dependence agree well with charge order in the Ni system, providing a direct experimental observation of this ordered phase.

Furthermore, the superstructure peak observed with resonant soft x-ray diffraction is much narrower in momentum space than probed by neutron diffraction, because the corresponding short penetration depth of soft x-rays together with the availability of well focussed x-ray beams makes this technique sensitive to slight local inhomogeneities of the doping level, which cannot be probed by bulk-sensitive techniques.

11:00 AM *Q1.7

Self-Diffusion in Chemically Homogeneous Multilayers using Nuclear Resonance and Neutron Reflectivity. Mukul Gupta1, Ajay Gupta2, Sanjoy Chakravarty2, T. Gubler1, H.-C. Wille3, O. Leupold2 and R. Rueffer2; 1Laboratory for Neutron Scattering, Paul Scherrer Institute, Villigen PSI, 2Swiss Light Source, Paul Scherrer Institute for DAE facilities, Indore, MP, India; 3European Synchrotron Radiation Facility, Grenoble, France.

Neutron reflectivity is a well-established technique for studying self-diffusion in chemically homogeneous system as neutron scattering length densities are different for isotopes of an element. For X-ray there is no contrast for a multilayer with isotopic abundance. Therefore, placing a Mossbauer active nuclei in a chemically homogeneous system, self-diffusion of the constituents can be probed using nuclear resonance scattering of Mossbauer active nuclei. In the present work, in an attempt to search for an alternative to neutron reflectivity, we have applied, for the first time, nuclear resonance reflectivity of synchrotron radiation source, for studying self-diffusion of iron in amorphous FeZr_{73}FeZr multilayers. It has been shown that both the techniques are complementary to each other and can be used with a unique depth resolution of the order of 0.1 nm. As compared with conventional techniques used for probing self-diffusion, neutron and nuclear resonance reflectivity techniques can be applied at significantly lower temperatures. On the basis of the obtained results the diffusion mechanism in amorphous chemically homogeneous multilayers is discussed in the present work.

11:15 AM *Q1.8


The advent of nanocarbons, from single- and multi-walled nanotubes to nanohorn, avails model systems of confined molecules on the nanoscale. Water encapsulated inside the quasi-one-dimensional channels of these materials is expected to exhibit anomalous behavior due to the unique geometry of the water molecules and the carbon atoms. We have employed neutron small-to-wide angle diffraction, quasielastic and inelastic scattering in conjunction with molecular-dynamics simulations to characterize the structures and dynamics of water adsorbed in open-ended single- and double-walled nanotubes over a wide range of spatial and temporal scales. We find that a square-ice sheet wrapped next to the inner nanotube wall and a water chain in the interior are the key structural elements of nanotubes-confined water. This configuration results in a hydrogen-bond connectivity that markedly differs from that in bulk water. This significantly scatters the hydrogen-bond network manifests in neutron experiments as shifts of the observed and simulated inter- and intra-molecular vibrations. The large mean-square displacement of hydrogen atoms observed experimentally and the strong anharmonicity inferred from simulations explain the fluid-like behavior at temperatures far below the freezing point of normal water. Work performed at Argonne National Laboratory is supported by the U. S. DOE-BES under contract No. W-31-109-ENG-38.

11:30 AM *Q1.9

The Coupling of Spin and Orbital Degrees of Freedom in a Layered Ruthenate: An Inelastic Neutron Scattering Study. Ray Osborn1, Peter Khalifah2, Stephen E. Nagler2 and Mark D. Lemmen2; 1Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 2Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

There is considerable evidence of the influence of orbital degrees of freedom on the magnetic properties of ruthenate compounds. The layered ruthenate compound, La2RuO4, features a first-order structural transition from a monoclinic to a triclinic phase, in which there are large changes in the Ru-O bond lengths [1], indicating a change in the orbital configuration of the 4d_{5/2} electrons. The magnetic susceptibility shows a sharp peak at the transition. Inelastic neutron scattering on both polycrystalline and single-crystal samples has shown that this is associated with the formation of a singlet ground state. Above the transition, the scattering is broad and quasielastic, consistent with the model for spin fluctuations within the S=1 ground state. Below the transition, a spin

Hence, QENS provides a direct measure of the conversion of free water to structurally/chemically bound water and to water constrained in the pores of the cement paste. Here we report the interaction of hydrating tricalcium and dicalcium silicates by QENS. Mixtures of synthetic tricalcium and dicalcium silicate were hydrated and their reaction mechanics explored as a function of mixture composition. The time-dependent free, constrained, and bound water results were analyzed. The complex interactions of the components during hydration gave interesting results, and demonstrated that the reaction proceeds non-linearly as a function of combinations of these two calcium silicates.

2:00 PM Q2.3 Neutron Spectroscopy of Carbon Nano-Materials. Alexander Keung Long1, Ching-Fan Shih1,2, Alexander P. Morozov1,2, and Christian J. Burnham1,2; 1IPNS, Argonne National Laboratory, Argonne, Illinois; 2MER Corporation, 7960 South Kolb Road, Tucson, Arizona; 3Henry Eyring Center for Theoretical Chemistry, University of Utah, Salt Lake City, Utah.

Although the existence of varieties of carbon nano-materials has been known for some time, the investigation of their vibrational spectra was mainly limited to the use of optical spectroscopy. In spite of the well-recognized advantages of inelastic neutron scattering (INS) technique, namely, unrestricted by the selection rules of infrared and Raman spectroscopy and accessible to all vibrational modes in the reciprocal space, so far this method was used for the study of only fullerenes and single-walled carbon nanotubes (SWNT). Here we present the INS measurements on a series of carbon nano-materials: SWNT (14 A diameter), double-walled carbon nanotubes (DWNT of 29 A diameters), and fullerene-C60 powders. We report the INS study of the vibrational spectra over a wide energy scale, from collective motions to localized atomic vibrations. The spectrum of nanohorns was similar to that of SWNT, and the latter one agrees with the main features reported in the literature. The INS spectrum of C60-powders and DWNT were very different compared to the spectra of both pure SWNT and pristine or polymerized fullerenes. The spectral intensity of the DWNT and C60-powders showed a strong reduction in the 'breathing' modes (normal to surfaces of C60 or SWNT molecules) over the range of 30-100 meV, and an increase at higher energies toward the 'tangential' modes around 110-160 meV. In addition, the vibrational bands of C60-peapods shifted to higher energies compared to that of C60-powders. These results indicate in general strong force fields associated with carbon-carbon interactions between the inner- and outer-walls in DWNT and between the fullerenes and nanotubes in C60-peapods. Work performed at Argonne National Laboratory is supported by the U. S. DOE-ES contract No. W-31-109-ENG-38.

2:15 PM Q2.4 Role of Glassy Dynamics in the Preservation of Proteins. Christopher L. Soles and Marcus T. Ciccarelli; Polymers Division, NIST, Gaithersburg, Maryland.

Proteins can be stored, and their biochemical functionality preserved for extended periods under non-physiological conditions, by enveloping them in certain viscous glass forming compounds such as trehalose or glycerol. However, the thermodynamic and kinetic variables that are critical to achieve optimum stabilization are not completely understood. While the ability of the glassy matrix to mimic water in terms of its thermodynamic interactions is realized, we focus on the effects of dynamics in the present. A strong correlation between incoherent neutron scattering and biochemical activity measurements indicates that an effective protein preservation matrix is also characterized by a strong suppression high-frequency (200 MHz and faster) dynamics. We contend that suppressing these nanosecond and faster motions in the glass impedes the protein dynamics at a slow time-scale, thereby conferring stability to the protein. To the best of our knowledge, this is the first direct evidence that the high frequency dynamics are relevant for protein preservation. This new perspective also sheds light on behavior of proteins in glass that was previously seen as aberrant; namely the observation that slower dynamics in glass mimic protein dynamic behavior in liquid versus glassy environments, and the failure of strict correlation between the glass transition temperature of a glass and its ability to serve as a protein preservation medium.

2:30 PM Q2.5 Dynamic Transition in Proteins and DNA: Role of a Solvent. Alexi Sokolov, Department of Polymer Science, The University of Akron, Akron, Ohio.

Hydrated proteins and DNA demonstrate a dynamic transition at temperatures Td 200-250K. It shows up as a sharp rise of mean-squared atomic displacement above these temperatures. Sharp slowing down of protein functions (rate of biochemical reactions) was observed at the same temperature range. These results suggest a direct relationship between the dynamic transition and onset of...
biochemical activities of proteins. However, the microscopic nature of the dynamic transition in biomolecules remains poorly understood. We analyze dynamics of DNA/D2O and lysozyme/D2O at different levels of hydration, and of lysozyme/glycerol using neutron scattering spectroscopy [1-3]. The results demonstrate that the dynamic transition in all these samples is related to a slow relaxation process that activates over a broad range of inorganic fillers and its relation to protein functions are discussed. We emphasize that Td observed for hydrated biomolecules (Td 200-230 K) and for proteins placed in glycerol (Td 270 K) coincides well with the temperatures of the dynamic arrest in the solvent molecules as estimated to be TC 220-230 K in water [4] and TC 270-290 K in glycerol [5]). This observation supports our earlier speculations [1,2] that the dynamic crossover of solvents controls the dynamic transition in biomolecular systems. The dynamic crossover of the solvent molecules leads to a suppression of large scale motions (the slow process) in biological molecules. The proposed microscopic mechanism of the dynamic transition is further supported by results of computer simulations [6,7] that demonstrate existence of dynamic arrest of the solvent molecules for the dynamic transition in proteins. These results suggest a way to control biochemical activity of biological macromolecules by modifying the solvent. 1. A.P. Sokolov, et al., J.Chem. Phys. 110, 7553 (1999). 2. A.P. Sokolov, et al., Nature 438, 296 (2005). 3. A.P. Sokolov, J Non-Cryst.Solids 235-237, 190 (1998). 4. M. Tarek, D. Tobias, Phys.Rev.Lett. 88, 138101 (2002). 5. A.L. Toumier, J. Xu, J.C. Smith, Biophysical J. 85, 1871 (2003). 3:30 PM Q2.6 A Small Angle Neutron Scattering Study of Protein Filaments F-actin, Jay X Tang1, Jorge Viamontes1, Qi Wen1 and Jyotsna La12, 1Physics, Brown University, Providence, Rhode Island; 2Argonne National Laboratory, Chicago, Illinois. The cytoskeletal protein actin self-assembles to form long and stiff filaments, F-actin, which serves essential functions in cells, such as control of cell shape, division, and motility. We have performed a small angle neutron scattering study with an aim to determine the hydrodynamic cross-sectional radius of F-actin in various ionic conditions. Reliable values were obtained using the contrast matching technique by measuring the scattering profile with various D2O/H2O mixtures. Since F-actin undergoes the isotropic-nematic (I-N) liquid crystal phase transition at temperatures lower than the dynamic crossover temperature, the scattering patterns of large ordered domains of F-actin were also obtained. Due to the large scattering area on the order of a square centimeter but on the other hand limited sample volume available, there has not been an effective way to align F-actin from solution. We used a neutron scattering technique that is suited for determination of the orientational order parameter. In all, our study demonstrates the applicability and limitations of the small angle neutron scattering study of solutions of protein filaments. 3:45 PM Q2.7 Large Scale Structures in Nanocomposite Hydrogels and Solutions, Gary L. Brown1, Paul D. Butler2 and Lionel Parcer3, 1Chemistry, Louisiana State University, Baton Rouge, Louisiana; 2NIST, Gaithersburg, Maryland. The structure and morphology of viscoelastic nanocomposite hydrogels is investigated by means of rheology and small-angle neutron scattering (SANS, USANS). Additional information from microscopy is used to better understand the structure. The length scales covered by these techniques provide information about short range structure as well as long range correlations. On a nanometer scale the clay can adsorb only a maximum amount of polymer till all the polymer molecules for the dynamic transition in proteins. These results suggest a way to control biochemical activity of biological macromolecules by modifying the solvent. 4:00 PM Q2.8 Structure and Dynamics of Polymer/inorganic nanocomposites, R. A. Narayanan1, P. Thiyagarajan1, B.J. Ash3, S.S. Sternstein3, A.J. Zhu1, Aimitabh Bansal1, L.S. Schadler4 and L. B. Lurio4, 1Intense Pulsed Neutron Source Division, Argonne National Laboratory, Lemont, Illinois; 2Institute for Biological Physics, Northern Illinois University, DeKalb, Illinois; 3Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, New York. Alumina/poly(methylmethacrylate) (PMMA) nanocomposites synthesized by in situ free-radical polymerization in the presence of 38 nm alumina nanoparticles exhibit a novel percolation-like transition at about 1 vol. % filler concentration [1]. This phenomenon is accompanied by a brittle-to-ductile transition with a large increase in the 'strain-to-failure'. In silica/polyvinylacetalate nanocomposites it is found that altering the interfacial bonding between the polymer and the filler by subjecting the various chemical treatments significantly affects their viscoelastic and reinforcement properties [2]. To understand the above phenomena and the molecular mechanisms, in general, responsible for the reinforcement of polymeric materials by nanophase separation of biomaterials. The evidence we have presented suggests that the dynamic crossover (dynamic arrest) in the pure solvents is reduced for the dynamic transition in the nanoparticles. The evidence supports our earlier speculation that the dynamic crossover of solvents controls the dynamic transition in biological macromolecules. We assume that the clay can adsorb only a maximum amount of polymer till all the polymer molecules for the dynamic transition in proteins. These results suggest a way to control biochemical activity of biological macromolecules by modifying the solvent. 4:15 PM Q2.9 Thin Polymer Film Structure using Resonant Soft X-ray Contrast Variation, Cynthia Welch, Rex Hjelm, E. Bruce Orler, Debra Wroblewski, Marilyn Hewley, Joseph Mang and Jeffrey Kortright, 1Los Alamos National Laboratory, Los Alamos, New Mexico; 2Lawrence Berkeley National Laboratory, Berkeley, California. The structure of thin (<1 μm) polyester urethane (PESU) films is analyzed with resonant x-ray scattering in the energy range near the carbon K absorption edge (280 - 310 eV), in this energy range, contrast variation results from changes in the atomic scattering factor across the carbon K to μa and μs absorptions. The PESU studied here is a segmented copolymer containing hard and soft segments of poly(ε-caprolactone) and poly(2,6-dimethyl-1,4-phenylene oxide), respectively. Extensive studies of thick films (μm) reveal that, in the bulk material, the segments phase-segregate into hard and soft segment-rich domains on the order of 20-30 nm. The hard domains act as network cross-links, giving the unique mechanical properties that make PESU films excellent materials for coatings, binder, and adhesive applications. Morphological studies of thin PESU films by small-angle scattering (SAXS) have proven difficult due to the lack of material in the beam, in many cases the weight between the hard and soft segment-rich domains. The strong interaction of low energy x-rays with light elements and the existence of light element resonances, particularly that of carbon, provide a path forward for structural studies of thin films that are appropriate to many PESU applications. Here we report our first attempts at using soft x-ray resonant scattering to study the structure of PESUs using the Advanced Light Source. Sample transmission spectra display resonances across the carbon absorption edge that scale with the PESU hard segment and thus aromatic content. Changes occur in the small-angle scattering at the same energies as these features. These observations show the existence of contrast variation between the aromatic and aliphatic carbons across the resonance that can be used in morphological studies. The scattering suggests that the domain structure in these thin films is not the same as that observed in the bulk materials. Thus far, polymer structure via resonant techniques has relied on high-energy x-ray resonances of heavy elements in chemically modified polymers. By extending this method to lower energy ranges associated with absorption edges of the light atoms, we significantly broaden this technique to polymer films. We have undertaken small-angle neutron scattering of thin polymer films without the need for chemical modification. 4:30 PM Q2.10 Microphase Separation and Rheology of Hydrophobically Modified Alkyl Acrylamides, Jun Tian1,2, Seery A. P. Thomas1,2 and Weiss A. Robert1,2, 1Chemical Engineering Department, University of Connecticut, Storrs, Connecticut; 2Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 3Chemistry, University of Connecticut, Storrs, Connecticut. The nanophase separation of random copolymer compositions of either N,N-dimethylacrylamide (DMA) or N-isopropylacrylamide (NIPA) and 2-(N-ethylfluorocanesulfonamido)-ethyl acrylate, FO_SA, was studied using small angle x-ray scattering (SAXS), transmission electron microscopy (TEM) and rheological measurements. SAXS
measurements showed that the copolymers exhibited a distinct scattering maximum when the FOSA composition is above 5 mol%, which indicated the nanophase separation in these copolymers. TEM showed that the FOSA-rich nanodomains was randomly dispersed in the FOSA-poor alkyl acrylamide matrix, which was consistent with the SAXS measurements. The fit of the SAXS data to the hard sphere model provided the domain size: the average radius of the FOSA nanodomain increased from 1.4 to 2.1 nm with increasing the FOSA content from 5 to 22 mol% for the DMA/FOSA copolymers, and it varied only slightly between 1.5 and 1.7 nm for NIPA/FOSA copolymer with FOSA content between 5 and 20 mol%. However, the microphase separation transition, MST, was not determined from temperature dependent SAXS. Rheological measurements showed that the principle of time temperature superposition, TTS, was stessfully performed for these copolymer melts, which may be due to the nature of weak segregation that provided the similar temperature dependencies of terminal relaxations for the FOSA-rich phase and the FOSA-poor alkyl acrylamide matrix. The broad microstructure distribution, the possible broad chain composition distribution, the random unit sequence along the polymer chain may also account for the applicability of the TTS.

SESSION Q3: Strain and Structure Observation with X-rays
Chair: Sudita Bhattacharya
Tuesday Morning, November 30, 2004
Hampton (Sheraton)

8:30 AM Q3.1
Crystallographic Texture in Pt/Si Structures Measured with Conventional and Synchrotron X-Ray Techniques.
Mark Vaudin1, Jan Hlavsky2 and Glen Fox2. 1Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland; 2XOR, Argonne National Laboratories, Chicago, Illinois.

The (111) fiber texture in 200 nm thin films of Pt deposited by magnetron sputtering on 150 mm (001) Si wafers has been characterized by various diffraction techniques, primarily x-ray. Parallel beam x-ray diffraction data were collected at the Advanced Photon Source using a CCD area detector. Each wafer was studied at two orientations 90° apart. Diffraction patterns were recorded over a square grid with a 2 mm pitch, yielding over 4000 texture measurements for a single Pt/Si wafer. In this way, the small variation in texture over the wafer, both in FHWM of the texture profile and orientation of the fiber texture axis, was very completely characterized. After cleaving the wafers into 100 nm square pieces, data were obtained using a 2-circle powder diffractometer divergent beam technique in which corrections were applied to omega scan data to account for defocusing and absorption. The comparisons between these data sets provide vital information in the development of a thin film texture standard. The relative accuracies and precision of the data sets give interesting insights into the relative strengths and the complementary nature of these two approaches to texture measurement. The utility of electron backscatter diffraction in texture measurements in highly oriented materials will be discussed.

8:45 AM *Q3.2
X-ray scattering: a wonderful tool to probe lattice strains in materials with small dimensions. Olivier Thomas, TECSEN UMR CNRS 6122, Univ. Paul Cezanne, Marseille Cedex 20, France.

X-ray diffraction was recognized from the early days as a very sensitive tool for atomic displacements. Indeed structural crystallography has been very successful in locating with great precision the position of atoms within an individual unit cell. In disordered systems it is the average structure and fluctuations about it that may be determined. In the field of real space the Bonse-Hart geometry may be used to evaluate elastic displacement fields. I will give examples from recent work where x-ray diffraction has been used to investigate average strains in lines, films or multilayers. In small objects the proximity of surfaces or interfaces may create very inhomogeneous displacement fields. X-ray scattering is again one of the best methods to determine such distributions. The need to characterize displacement fields in nanostructures together with the advent of third generation synchrotron radiation sources has generated new powerful methods (x-ray diffraction, micro-diffraction, transmission electron microscopy, scanning electron microscopy). I will review some of the recent and promising results in the field of strain measurements in small dimensions via X-ray diffraction.

9:15 AM Q3.3
Large-Scale Morphology of Dispersed Layered Silicates.
Dale S. Schaefer1,2, Ryan S. Justice1, Hilmar Koerner1, Richard Vinz1, Chunhui Zhao2 and Mingshou Yang2. 1Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; 2MLBP, Air Force Research Laboratory, WPAFB, Ohio.

In spite of concerted international effort to elucidate the dispersion of layered silicates in solution and solid matrices, there is minimal agreement regarding the interpretation of diffraction patterns, including even a consistent definition of exfoliation. X-ray diffraction is widely used to determine the dispersion (intercalation, exfoliation) of layered silicates through the position and width of the Bragg reflections from the layered structure. Such measurements show information on large-scale layer-layer correlations, local fluctuations in layer orientation, and hierarchical morphology. Here we discuss the use of small angle x-ray scattering and light scattering to characterize nanostructured materials with small dimensions via X-ray diffraction, micro-diffraction). We will review some of the recent and promising results in the field of strain measurements in small dimensions via X-ray diffraction.

9:30 AM Q3.4

This talk will focus on newly developed synchrotron techniques to measure strains and stresses in small volumes. Laue microdiffraction, on one hand, allows for the determination of all 5 components of the deviatoric strain tensor smaller than 20 nm. Examples of application of these techniques will be given. On the other hand, the newly developed in-situ technique for thin film tensile testing, on the other, enables the measurement of stress-strain curves for metal films as thin as 20 nm. Examples of application of these techniques will be given. The full size range from 1 nm to more than 1 micrometer within a single scan. While the USAXS measurement geometry is inherently limited to the maximum size due to limitations in the spatial extent of the coherent scattering region, the micrometer scale regime can be extend the maximum feature size into the micrometer scale regime. Ultrasmall-angle x-ray scattering (USAXS) at a 3rd generation synchrotron such as the Advanced Photon Source (APS) can access the full size range from 1 nm to more than 1 micrometer within a single scan. While the USAXS measurement geometry is inherently limited to the maximum size due to limitations in the spatial extent of the coherent scattering region, the micrometer scale regime can be extended to the maximum feature size due to the integration of the Bonse-Hart geometry. I will review some of the recent and promising results in the field of strain measurements in small dimensions via X-ray diffraction.

11:00 AM Q3.6
In-situ Deformation Studies at the Swiss Light Source. Helena Van Swygenhoven, ASQ/NUM, Paul Scherrer Institute, PSI-Villigen, Switzerland.

X-ray diffraction profile analysis is a well known technique for microstructural analysis, where the broadening of the peaks results from limitations in the spatial extent of the coherent scattering volume. In our case the grain size and the presence of inhomogeneous strain. Thanks to the high intensity of the Swiss Light Source and the development of a microstrip detector covering a diffraction angle of 40 degrees with an angular resolution of 0.0037 degrees, it has been possible to develop a new in-situ technique that allows peak profile analysis of several Bragg diffraction peaks during tensile deformation. This talk will show several interesting results obtained during in-situ deformation studies such as the reversibility of
the peak broadening during plastic deformation of electrodoped nanocrystalline Ni (Science 304(2004)273) and the applicability to measure elastic and plastic properties free standing thin films of a few microns and less. Furthermore, it will be shown how X-ray spectra derived from atomistic simulated nanocrystalline samples can help understand measured diffraction spectra.

11:15 AM Q3.7

A planar magnetron sputter deposition system was constructed on top of a XRD diffractometer for real-time investigation of thin film nucleation and growth, using a 1-D and a 2-D area detector. A cylindrical magnetron sputter deposition system, which allowed substrate temperature control, was used to complement the in-situ system. Depositions were made on glass, silicon wafer, and Al2O3 under various deposition conditions. Results from our current investigation are summarized: 1) Krypton sputter gas promotes bcc phase over tetragonal phase tantalum, when compared to argon sputter gas. 2) Higher substrate temperature promotes bcc phase over tetragonal phase tantalum film. 3) Substrate species affect phase of tantalum film during nucleation and growth. However, film can change phase during growth with no apparent external interference. 4) In the range of 5-40 Torr and 75 watts, phase is not sensitive to gas pressure or plasma power. 5) Sputter gas pressure greatly affects deposition rate and film density. 6) Sputter pre-clean of substrates prior to sputter deposition improves film adhesion to the substrate. 7) A thin sputter-deposited chromium interface layer between tantalum and substrate steel improves film adhesion to the substrate.

11:30 AM *Q3.8
Anisotropic USAXS from Stretched Filled Polymers. Thomas Rieker, Pete Jemain, and Jan Ilavsky; Div. of Materials Research, National Science Foundation, Arlington, Virginia; Argonne National Laboratory, Laboratory for Advanced Photon Source, Argonne, Illinois.

The morphology of stretched carbon black filled polymer samples was studied using anisotropic Ultra Small-Angle Scattering (USAXS). Experiments were conducted using the 2-D Bonse-Hart instrument at the APS. The utility of the 2-D Bonse Hart and preliminary results will be discussed.

2:15 PM Q4.3
Resonant Soft X-Ray Emission and Inelastic X-Ray Scattering Study of Electronic Structure near the Fermi Level in the Organic Semiconductor Copper Phthalocyanine. James E. Downes, Corkac McGuinness, Peter-Anders Olofsson, Timothy Learmonth, Yifeng Zhang, and Kevin E. Smith; Department of Physics, Boston University, Boston, Massachusetts; School of Chemical and Physical Sciences, Victoria University, Wellington, New Zealand; Department of Physics, Trinity College Dublin, Dublin, 2, Ireland.

We report a synchrotron radiation-excited resonant soft x-ray emission (SXE) spectroscopy study of the electronic structure near the Fermi level of thin films of the prototypical organic semiconductor copper phthalocyanine (CuPc) [1]. SXE measures directly the element-resolved partial density of states (PDOS) in materials. At resonance with selected core levels, SXE measures the PDOS associated with particular chemical sites or environments, and resonant inelastic x-ray scattering (RIXS) features can be observed. We will discuss the application of resonant SXE and RIXS in the study of CuPc. Our results are in excellent agreement with theory, but differ significantly from previously published x-ray emission and photoemission results. The CuPc films were discovered to be highly susceptible to synchrotron radiation beam damage. We successfully circumvented this effect by continuous translation of the films during measurement. Resonant SXE spectra from undamaged samples show spectral features near the Fermi level that have not been observed from damaged samples. These states are predicted to exist, but have not yet been observed by either photoemission spectroscopy or soft x-ray emission spectroscopy. Since it is the properties of the highest occupied molecular orbital (HOMO) states that are of most interest, the ability of resonant SXE to accurately measure these states is significant, as is our discovery of SXE studies of organic semiconductor doms are dominated by beam damage effects. This application of resonant SXE has important consequences for the determination of band gap energies in organic molecular crystal systems, since it allows accurate measurement of the electronic structure. Supported in part by the donors of the Petroleum Research Fund, administered by the ACS, and by the NSF under DMR-0309490. Our synchrotron spectrometer is funded by the U.S. ARO under DAAD19-01-1-0364 and DAAH04-95-0014. Experiments were performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences. 1. J. E. Downes, C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).
The properties of the Na$_2$Co$_3$O$_7$ class of materials are very interesting from a number of standpoints. It is a triangular lattice of spin-1/2 ions, and the superconducting transition temperature is very high. The electronic properties of such materials have been studied extensively, and significant differences are found, particularly for the O 2p states. Low energy excitations across the gap are observed as loss features in the scattering of phonons at the V 2p/2 absorption edge. Both dipole forbidden 3d-3d excitations and O 2p - V 3d charge transfer excitations are observed. The relationship of these excitation energies to those observed in vanadium oxide crystals will be explored. Supported in part by the Petroleum Research Fund, administered by the ACS, by the U.S. ARO under DAAD19-01-1-0364 and DAAH04-95-0014.

We demonstrate single-shot x-ray laser induced time-of-flight photoelectron spectroscopy on semiconductor and metal surfaces with picosecond time resolution. The LIML group at the Stanford Synchrotron Radiation Light Source has recently shown that time-resolved x-ray photoemission spectroscopy for single-shot tabletop x-ray laser source provides the necessary high photon flux (>10$^{12}$/pulse), monochromatic, picosecond pulse duration, and coherence for probing ultrafast changes in the chemical and electronic structure of these materials. Shocked and heated materials, time-resolved x-ray laser induced photoemission results for ultra-thin Cu will be presented. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

We report a synchrotron radiation excited resonant soft x-ray emission spectroscopy study of the electronic structure of thin films of the organic semiconductor vanadium oxide phthalocyanine (VOPc) measured using high resolution resonant soft X-ray emission spectroscopy. Yufeng Zhang, Timothy Leamouth, Lukasz Plucinski, Shancai Wang, Sarah Bernardis, Cian O'Donnell and Kevin E. Smith; Physics Department, Boston University, Boston, Massachusetts.

We report a synchrotron radiation excited resonant soft x-ray emission (SXE) spectroscopy study of the electronic structure of thin films of the organic semiconductor vanadium oxide phthalocyanine (VOPc). SXE measures directly the element-resolved partial density of states (PDOS) in materials [1]. At resonance with selected core levels, SXE measures the PDOS associated with particular chemical sites or environments, and resonant inelastic x-ray scattering (RIXS) features can be observed that are due to excitations from filled valence states to empty conduction states [2]. We have recently reported a resonant SXE study of thin films of copper phthalocyanine, CuPc, and showed that by using this resonant SXE spectroscopy and x-ray excited valence photoemission spectroscopy near the Fermi level in organic systems can be accurately measured [3]. We present here the results of a resonant SXE measurement of the V, O, and C PDOS in VOPc, as well as report the observation of RIXS excitations from occupied to unoccupied states. The VOPc films were grown in-situ at beamline X1B at the National Synchrotron Light Source. Films were grown in a ultra-high vacuum organic molecular beam deposition system, and transferred under vacuum to the spectrometer. With our earlier study of CuPc [3], the VOPc films were discovered to be highly susceptible to synchrotron radiation beam damage. We successfully circumvented this effect by continuous translation of the films during measurement. We find that the measured 0 2p PDOS for VOPc differs from that of CuPc, and will discuss the possible origins of this result. The measured O 2p and V 3d PDOS can be compared directly to those obtained from a variety of vanadium oxides, and significant differences are found, particularly for the O 2p states. Low energy excitations across the gap are observed as loss features in the scattering of phonons at the V 2p/2 absorption edge. Both dipole forbidden 3d-3d excitations and O 2p - V 3d charge transfer excitations are observed. The relationship of these excitation energies to those observed in vanadium oxide crystals will be explored. Supported in part by the Petroleum Research Fund, administered by the ACS, by the U.S. ARO under DAAD19-01-1-0364 and DAAH04-95-0014.

We demonstrate single-shot x-ray laser induced time-of-flight photoelectron spectroscopy on semiconductor and metal surfaces with picosecond time resolution. The LIML group at the Stanford Synchrotron Radiation Light Source has recently shown that time-resolved x-ray photoemission spectroscopy for single-shot tabletop x-ray laser source provides the necessary high photon flux (>10$^{12}$/pulse), monochromatic, picosecond pulse duration, and coherence for probing ultrafast changes in the chemical and electronic structure of these materials. Shocked and heated materials, time-resolved x-ray laser induced photoemission results for ultra-thin Cu will be presented. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.
experimentally and theoretically. Understanding the oxidation mechanism is important for practical purpose in many cases, since thin oxide films can act as passive layers, and protect metals from corrosive environments. Several growth models have been proposed to explain oxidations at low temperatures or under electrochemical environments where thermal diffusion of metallic cations and oxygen anions is limited. Experimentally, however, only limited data are available due to difficulties in measuring in situ the growth kinetics of very thin passive oxide films of a few nm thick. In this work, we investigate the growth kinetics of passive films in iron and stainless steel (Fe-16.1%Cr) substrates in pH 8.4 borate buffer solution using in situ specular x-ray reflectivity. The oxide growth rate decays exponentially with increasing oxide thickness consistent with the point defect model in which the electric field in the oxide is maintained constant during growth. In stainless steel, however, the electric field depends strongly on the applied potential indicating that the oxide properties change as the applied potential varies. Using the electric field and the observed saturation oxide thickness in a quasi-static state, we examined the potential drop across the dielectric/metalide interface, in the oxide, and at the oxide/solution interface.

Q5.4 SANS techniques to study cavitation in Zr based superplastic materials. Steven Van Petegem, A. Chokshi, S. Ghosh, J. Stahn and H. Van Swygenhoven; 1NUM/ASQ, Paul Scherrer Institut, Villigen PSI, Switzerland; 2NUM/LNS, Paul Scherrer Institut, Villigen PSI, Switzerland; 3Department of metallurgy, Institute of Science, Bangalore-560012, India.

The ability of some fine-grained materials to exhibit very large elongations to failure, termed superplasticity, is being explored commercially to form complex-shaped components. Recently, the observations of large ductility in ceramics has attracted attention, since superplastic forming may offer a means to form ceramics that are usually considered brittle. It is well recognized that most superplastic material cavitate during deformation, and excessive cavitation is often a leading cause for premature failure in superplastic materials. Cavitation failure is particularly important in superplastic ceramics, and there have been several studies of cavitation at large strains in superplastic ceramics. Most of these studies relate to concurrent cavitation at large strains of >100%, or are restricted to measuring cavities with dimensions greater than one micron. Here we present a study of the early stages of cavitation damage in 3 mol% yttria stabilized tetragonal zirconia (3YTZ) and zirconia-alumina. Therefore we use a combination of SANS, USANS, SEM, optical microscopy and density measurements, which allows us to investigate cavity sizes from the nanometer to the micrometer range. The results are compared with existing theoretical models for cavity growth.


Reorientation of polymer materials under the influence of external fields usually appears on time scale much longer than those associated with the dynamics of single macromolecules, owing to the presence of mesoscopic ordering at length scales between 1 and 1000 nm. The network structures, formed by self-assembly of pre-organized macromolecules in solution, represent a rather complex case since in such systems a (re)ordering is strongly affected by the presence of physical crosslinks. Time-resolved small angle x-ray scattering experiments allow insight, not only into the nature of the ordered macromolecular structures but provide moreover the possibility to directly assess the evolution in overall arrangement under the influence of shear or uniaxial deformation.

Q5.6 A View on Dendrimer-Based Nanoassemblies with Small Angle Scattering. Ralf Kleppinger, 1Michel Koch and Kell Mortensen; 1DSM Research, Geleen, Netherlands; 2EMBL Hamburg, Hamburg, Germany; 3RISO National Laboratory, Roskilde, Denmark.

An interesting aspect of highly branched macromolecules like dendrimers or hyperbranched polymers is their ability to incorporate low molar mass guest molecules into their three-dimensional structures. However, potential bioapplications of such systems require functionalization of the host system, aiming towards improved
biocompatibility. The resulting linear-dendritic hybrids are efficient host systems which can accommodate a variety of guests. Small angle X-ray and neutron scattering experiments were used to provide information regarding the global arrangement of such complexes.

Q5.7 TRANSFERRED TO Q5.2

Q5.8

Real-Time X-Ray Scattering Studies of P(VDF-TrFE)
Copolymer: Comparison of Bulk Film and Solution Grown Crystals. Bedirje Seyhan Ince and Peggy Cebe; Physics Department, Tufts University, Medford, Massachusetts.

Simultaneous real-time wide and small angle X-ray scattering (WAXS, SAXS) were performed on random copolymers of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] in composition 75 mol% VDF. We investigate the kinetics of the paraelectric to ferroelectric phase transition using WAXS. From SAXS we obtain the kinetics of lamellar structure development. SAXS intensities are analyzed using the one-dimensional electron density correlation function, and the interface distribution function, to yield the SAXS parameters relating to a model of one-dimensional lamellar stacks. Comparison is made between bulk films, cast from dimethylacetamide solutions, and solution grown crystals (SGCs). SGCs are prepared from 9/1 (weight%) monochlorobenzene/dimethylformamide dilute solution at polymer concentration of 0.01% - 0.05% by weight, followed by isothermal crystallization. At low polymer concentrations the SAXS on the bulk film reveals morphology comprising lamellar bundles and larger scale domains. SAXS analysis shows that in SGCs the Bragg spacing is shorter indicating much thicker lamellae, in both paraelectric and ferroelectric phases, compared to bulk film. Morphology studies are presently ongoing to compare structural information on the SGCs with that obtained on the bulk film.

Q5.9


Small-angle x-ray scattering (SAXS) measurements have been performed to investigate He bubble formation in borosilicate glass. The purpose of the experiments is to better understand the performance of glass as a radionuclide waste storage medium. The BESIRC 12-1D line at the Advanced Photon Source was used for the SAXS measurements. The measured Q range extended from 0.004 to 0.4 Å⁻¹. Two sets of helium implantations were performed, at low energy (5 keV) and at high energy (1-2 MeV), over a dose range of 10E14 to 10E16 ions/cm² for each set. The local concentration associated with this dose range spanned the solubility limit (approx. 100 appm) of He in glass at room temperature, extending from approximately 50 appm to 104 appm. The low-energy set of implantations was performed to study the influence of the free surface on He bubble formation. Some low-concentration samples were selected for low-temperature annealing (T < 200 °C). This annealing procedure simulated decay heat, thereby facilitating He bubble formation at or below the room-temperature solubility limit. In addition, some of the low-energy implantation samples were bombarded with high-energy Xe ions to simulate the heavy ion recoil that occurs during alpha decay. The SAXS response at high Q (Q < 0.4 Å⁻¹) exhibited a broad interference peak that grew in magnitude and shifted to lower Q values as the local He concentration increased. Discussion of the results will focus on the effect of a free surface and low temperature annealing on He bubble formation, and also on He bubble stability during Xe bombardment. Work supported by the DOE NEER program under grant DE-FG07-01ID14121.

Q5.10 TRANSFERRED TO Q5.7

Q5.11

In-situ SAXS Study of Cold-Crystallized Isotactic Poly(styrene): Confinement Within a Self-Similar Structure. Hui Xu and Peggy Cebe; Physics Department, Tufts Univ., Medford, Massachusetts.

The crystalline lamellar structure of isotactic poly(styrene) (IPS) was investigated during crystallization by in-situ small angle X-ray scattering (SAXS) using synchrotron radiation. IPS was cold-crystallized by heating from the glassy amorphous state. Heat capacity analyses and wide-angle X-ray scattering results show that the cold-crystallized IPS comprises three fractions: mobile amorphous, rigid amorphous, and crystals. SAXS parameters of long period, scattering invariant, and partial structure factor were used to analyze the one-dimensional electron density correlation function and/or interface distribution functions. Temperature dependent changes in these parameters were correlated to changes in the glass transition temperature, Tg, during crystallization. After spherulite impingement, Tg increases dramatically. More importantly the cooperative length, l, which indicates the spatial limitation on the large mode length of the glass transition, gets smaller during crystallization. Cold-crystallization of IPS leads in reduction of mobility: the free-volume-like amorphous phase becomes confined in a self-similar structure of IPS lamellae during crystallization, leading to the formation of the rigid fraction, broadening of the relaxation, and increase in Tg. Finally, SAXS results show that the mobile amorphous layer thickness is larger than cooperative length l, while the rigid amorphous layer thickness is smaller than l.

Q5.12

Neutron Reflectivity Study of Lipid Membranes Assembled on Ordered Nanocomposite and Nanoporous Silica Thin-Films. Devanil A. Doval1, Andrew M. Dattelbaum1, Erik B. Watkins1, Jaroslav Majewski1, Andrew P. Shreve2 and Atul N. Parikh3; 1Los Alamos National Laboratory, Los Alamos, New Mexico; 2University of California-Davis, Davis, California.

Ordered nanocomposite and nanoporous silica thin-films are promising platforms for supporting lipid membrane architectures that mimic biological systems. In this study we have systematically investigated the viability and the interfacial characteristics of phospholipid membranes forming on ordered thin films, on the use of neutron reflectivity. The non-destructive nature and long penetration depth of neutrons (compared to x-rays) makes neutron reflectivity an ideal technique to study the soft silica film-membrane and membrane-water interfaces. Silica thin films were prepared via an evaporation induced self-assembly process, which involves the hierarchical organization of organic surfactant and inorganic silica building blocks. POPC (1-Palmitoyl-2-Oleoyl-sn-Glycerol-3-Phosphocholine) lipid membranes were then deposited on the silica thin-film surfaces by vesicle fusion. The silica surfaces were also modified with a self-assembled silane monolayer prior to lipid membrane formation. We have studied the influence of the silica thin-film surface i.e. its hydrophobicity and surface charge on the vesicle fusion process and the structure of deposited membranes. A detailed analysis of all the thin-film/lipid membrane interfaces and structures formed will be presented. This work was supported by Los Alamos National Laboratory under DOE contract W7405-ENG-36, and by the DOE Office of Basic Energy Sciences.

Q5.13

Effects of Ca-Doping on Crystal Structure of BaTiO3. Young-Gi Jung1, Baeukyun Lim2, Sangkyun Lee3 and Jeongwook Kim2; 1Analysis Group, Central Institute of R&D, Samsung Electro-Mechanics Co., Suwon, South Korea; 2Chip Materials Lab, Samsung Electro-Mechanics Co., Suwon, South Korea.

Recent high capacitance MLCCs (multi-layer ceramic capacitor) consist of BaTiO3 ferroelectric material for dielectrics and Ni base metal for inner electrodes. For the mass production of high capacitance MLCCs, high dielectric constant BaTiO3 (BT) powders with fine grains are required. MLCCs have to be cofired in a reducing atmosphere to prevent from oxidization of Ni electrode, which results in poor insulation resistance of BaTiO3 ceramics. Therefore additive doping of BaTiO3 is of great importance for chip products with high reliability in severe environments. At present, Ca becomes one of the important elements for achieving the high reliability in MLCC industry. BaTiO3 ceramics have some degree of grain size dependence in dielectric properties. For the measurement of BaTiO3 dielectric properties at the powder manufacturing steps, tetragonality defined by c/a lattice ratio is widely used. However, because of broadening of x-ray peaks, nano BaTiO3 powders with Ca dopant (BCT) are difficult to evaluate the dielectric properties in the stage of producing process. In this research, the influences of solid solution Ba1-xCaTiO3 on crystal structure are investigated using x-ray diffraction. Additionally, details for controlling experimental parameters in x-ray optics are provided, as well as accuracy in evaluation of tetragonality. After XRD analyzed, the crystal properties of structure such as strain, crystallite size, position, could be evaluated. By these analysis, the electrical properties of BCT powders could be related to the crystal properties of structure.

Q5.14

X-Ray Study of the Confinement of Silver Chalcogenide Inside Mesoporous Silica. Marie-Louise Saboungi1, 2, Vincent Leon2,2, Yang Ren and Atul N. Parikh3; 1IPNS, Argonne National Laboratory, Argonne, Illinois; 2CRMD, CNRS, Orleans, France.

Inside Mesoporous Silica.
Silver chalcogenides such as Ag$_2$Se and Ag$_2$Te are known to be non-magnetic at room temperature without displaying significant magnetoresistance. However, altering the stoichiometry to accommodate a small amount of surplus silver, the electrical resistance of Ag$_{2+x}$Se and Ag$_{2+x}$Te (with $x = 0.01$) became very sensitive to magnetic field up to 60 Tesla. Furthermore, this giant magnetoresistance exhibits a nearly linear increase of the resistance with increasing applied magnetic field without apparent saturation. Thus silver chalcogenides may be an attractive candidate as magnetic random access memory (MRAM). Our work in this field of material science in an inorganic matrix to make a nanocomposite. The choice of silica is the most appropriate since silica is chemically inert and it has been shown in the case of selenium based materials that interactions between silica and selenium are very weak and that confinement preserves their semi-conducting properties. The method we have used to confine nanoparticles inside silica is the synthesis of silver chalcogenide directly inside the pores of mesoporous silica, presenting an array of possibilities with different sizes for this kind of material. Ag$_2$Se, after impregnation of a silver ions solution into silica, a selenium ions solution is introduced. The existence of nanocrystalline silver selenide has been confirmed using synchrotron radiation X-ray diffraction. The observed diffraction peaks correspond well to the orthorhombic structure of Ag$_2$Se.

Q5.15
Energy Controlled X-ray Filter for Energy Dispersive X-ray Reflectometry, Toshikazu Horii, Keitaro Kago and Kazumi Matsusige; Electronic Science and Engineering, Kyoto University, Kyoto, Japan.

X-ray reflectometry (XR) is a technique to determine the thickness, the surface and interface roughness and the electron density of thin films. There are two measurement techniques; one is angle dispersive X-ray reflectometry (ADXRR) and another is energy dispersive X-ray reflectometry (EDXR). In the former, the incident beam is the monochromatized X-ray; it is reflected at the surface and interface of a thin film and detected by a scintillation counter. In this technique, the incident and reflection angles are scanned to change the scattering vector of the X-ray. On the other hand, in the latter, the incident beam is a white X-ray; the X-ray reflected by the thin film is detected by a solid state detector (SSD). By the SSD, the X-ray reflection intensity is counted for every energy under a fixed angle. The same information on the structure of the thin film can be obtained both by ADXRR and EDXR. In EDXR, the totally reflected X-rays with high intensity in the energy range below the critical energy and the X-rays with low intensity in the higher energy range are entered into the SSD at a time or detectable area. Therefore, the reflected X-ray in the higher energy is hardly detected precisely. To solve this problem, we invented the reflection-transmission type X-ray filter. This filter consists of the substrate of low attenuation coefficient and the thin film of high attenuation coefficient. Our work in this field is to form this kind of material into a nanocomposite. The choice of silica is the most appropriate since silica is chemically inert and it has been shown in the case of selenium based materials that interactions between silica and selenium are very weak and that confinement preserves their semi-conducting properties. The method we have used to confine nanoparticles inside silica is the synthesis of silver chalcogenide directly inside the pores of mesoporous silica, presenting an array of possibilities with different sizes for this kind of material. The existence of nanocrystalline silver selenide has been confirmed using synchrotron radiation X-ray diffraction. The observed diffraction peaks correspond well to the orthorhombic structure of Ag$_2$Se.

Q5.16
X-ray Nanoplasma Instruments and Tools, Scott Bloom, Harry Rieger and James Alwan; JMAR Research, San Diego, California.

Nanoscale materials are currently being aggressively pursued by both military and non-military R&D groups. Applications of these materials are wide ranging and potentially revolutionary. In order to develop such materials, the design, diagnostic testing, accurate, sensitive, chemical analysis on the spatial scale of the nanomaterial itself are required. There are currently many materials analysis techniques available to look into sub-cellular and individual atom sites. While these techniques are quite reliable and sensitive they currently do not have the capability to sample materials, particularly in-situ, on the spatial scales required for nano technology. In order to accomplish this objective, JMAR has developed a new tool for use in an innovative nanoplasma technique based on our expertise in producing soft X-rays using a laser produced plasma. Soft X-rays have wavelengths in the range of 1-15 nm and therefore the diffraction limited spot size of focused X-rays can be as small as 1.2nm. While the radiation wavelength, or less than 20 nm spot size. The other key piece of this technique is having an X-ray source that is bright enough that when focused to a 10-30 nm spot size will deliver enough power per unit area to pattern a sample and heat the material for the desired plasma. A JMAR soft X-ray source has demonstrated more than 20 W of X-ray power into 2π sr, focusing a small collected solid angle of this X-ray radiation is more than enough power to form a very hot plasma that emits a range of UV through IR that can be collected and analyzed on a conventional optical spectrometer. The technique is very similar to LIBS, Laser Induced Breakdown Spectroscopy except here the radiation used to form the plasma is soft X-rays (200eV to 2 keV). Furthermore, the focused spot size is much smaller in diameter and therefore suitable for studying materials at nanoscale spatial resolutions. Other diagnostic techniques such as TOF-MS, XFS and PEEM can be used as well. In addition to diagnostic capabilities this technique can also be used as a tool to form structures at nanometer scale resolution. Since the plasma is formed by ablating the target material with x-rays the target can be patterned or nanomachined using the plasma itself. It should be possible to pattern nanocrystals under the nanoplasma. Finally in analogy to plasma assisted CVD processes, organometallic vapors could introduce into the sample chamber such that the nanoplasma locally plates out specific species of metals or organometallics (up to 200 W at 100 $\mu$m spot size for several hours). This paper presents a design for a nanoplasma instrument, predicted performance parameters will be presented, and development issues identified and discussed.

SESSION Q6: Novel Materials and Nanoscience: Insights from X-rays and neutrons
Chair: Valeria Gabriela Stoleru
Wednesday Morning, December 1, 2004
Hampton (Sheraton)

8:30 AM Q6-1
Structure of Optical Recording Material Ge$_2$Sb$_2$Te$_5$ Studied by Pulsed Neutron Diffraction, Shin-ichi Shamoto$^1$, Toshiyuki Matsuasa$^2$, Noboru Yamada$^3$, Thomas Proffen$^4$, James W. Rieger$^5$, and James Alwan$^6$; JMAR Research, San Diego, California.

The Ge$_2$Sb$_2$Te$_5$ (GST) compound has been widely used as a high-speed phase-change material such as DVD-RAMs. The study of these crystal structures becomes an important subject for the improvement of important performance such as the effective energy conversion from light to heat in a limited area. We have studied the crystalline compound by Rietveld and atomic pair distribution function (PDF) analyses. Within the Rietveld analysis, the space group of Pm-3m gives us the best result. If the average crystal structure was intrinsic, the first nearest neighbor peak in the G(r) (PDF) should be a broad simple Gaussian. The first nearest neighbor peak observed by the PDF analysis, however, had a complex structure. It cannot be described by one broad peak expected from the Rietveld analysis. Since 4(a) site is entirely occupied by tellurium atom, only Ge-Te and Sb-Te bonds appear in the first peak. The obtained G(r) pattern was successfully fitted under the following restriction: Rwp = 10.8% and Rs = 6.0%.

8:45 AM Q6-2
Small angle neutron scattering (SANS) and x-ray reflectivity (XR) as complimentary methods to characterize porous films containing meso-pores, Bryan D. Vogt$^1$, Rajaram A. Pai$^2$, Hae-Jeong Lee$^3$, Christopher L. Soles$^4$, Wen-li Wu$^5$, Eric K. Lin$^6$ and James J. Watkins$^7$; 1Polymers Division, NIST, Gaithersburg, Maryland; 2Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee; 3Energy Controlled X-ray Filter for Energy Dispersive X-ray Reflectometry. Toshihisa Horiuchi, Keitaro Kago and Kazumi Matsusige; Electronic Science and Engineering, Kyoto University, Kyoto, Japan; 4Panasonic Ltd., Moriguchi, Osaka, Japan; 5LANSE, Los Alamos National Laboratory, Los Alamos, New Mexico; 6IPNS, Argonne National Laboratory, Argonne, Illinois; 7Center for Neutron Research, National Institute of Standard and Technology, Gaithersburg, Maryland; 8University of Tennessee, Knoxville, Tennessee.

The Ge$_2$Sb$_2$Te$_5$ compound has been widely used as a high-speed phase-change material such as DVD-RAMs. The study of these crystal structures becomes an important subject for the improvement of important performance such as the effective energy conversion from light to heat in a limited area. We have studied the crystalline compound by Rietveld and atomic pair distribution function (PDF) analyses. Within the Rietveld analysis, the space group of Pm-3m gives us the best result. If the average crystal structure was intrinsic, the first nearest neighbor peak in the G(r) (PDF) should be a broad simple Gaussian. The first nearest neighbor peak observed by the PDF analysis, however, had a complex structure. It cannot be described by one broad peak expected from the Rietveld analysis. Since 4(a) site is entirely occupied by tellurium atom, only Ge-Te and Sb-Te bonds appear in the first peak. The obtained G(r) pattern was successfully fitted under the following restriction: Rwp = 10.8% and Rs = 6.0%.
Ordered mesoporous films were synthesized using acid-doped amphiphilic block copolymer film templates and subsequently infusing the film with silica precursors in supercritical carbon dioxide. The pore structure and distribution in these films was probed using x-ray reflectivity measurements. The presence of long-range mesoporous order was confirmed by x-ray scattering (SANS). The x-ray scattering corresponding to micropores from the removal of the hydrophilic polymer phase. The wall density is defined by the null contrast point determined through contrast variation capillary condensation measurements. The fraction of micropores in the film can be determined from these contrast variation measurements. XRF probes the average electron density of the film - the density is varied through capillary condensation filling of the pores with toluene. The wall density and total porosity can be determined from the XR measurements. From the XR measurements, the mass uptake of the toluene probe as a function of toluene partial pressure is directly determined from the shift in the critical edge. This is similar to the N2 adsorption porosimetry data, but uses significantly less material and allows for thin film characterization. This mass uptake data can be converted into a pore size distribution with the appropriate model. Additionally from the adsorption and desorption branches, the microporosity can be estimated. From SANS and XR, the pore structure and distribution can be determined non-destructively. Comparison of results between the two measurement methods will be discussed.

9:00 AM **Q6.3**

Magnetic Ferroelectric Perovskite Rare-Earth Manganites, Tatsuo Kiyama, Takayuki Kotera, Akihiro Tanaka, and Hirofumi Shigeta. The relationships among magnetism, lattice modulation, and dielectric properties have been investigated for perovskite rare-earth manganites, $\text{RMnO}_3$ ($\text{R} = \text{Eu, Gd, Tb}, \text{and Dy}$). At room temperature, the $\text{RMnO}_3$ have the $Pbnm$ orthorhombic structure which is centrosymmetric. These compounds show a transition to an incommensurate lattice structure at the Néel temperature ($T_N \approx 530K$) for sinusoidal antiferromagnetic ordering and subsequently undergo an incommensurate-commensurate phase transition. Dielectric anomalies were observed at the respective transition temperatures ($T_D$, $T_s$, and $T_D^*$) and $T_J$, and found that the incommensurate-commensurate transition is accompanied by a ferroelectric transition, associated with a lattice modulation in the commensurate phase. This close relationship between lattice modulation and ferroelectricity is common to so-called improper ferroelectrics such as $\text{K}_2\text{SeO}_3$. The lattice modulation in the rare-earth manganites originates in magnetic interactions through lattice modulations. Supporting this view, the magnitude and direction of ferroelectric polarization can be tuned by the application of magnetic field in these manganites. We will present the giant magnetoelectric and magnetocapacitance effects observed in $\text{RMnO}_3$.

9:30 AM **Q6.4**

Retro-Novel-lattice Space Imaging of X-ray Intensities Diffracted from Nanowires, Osamu Sakata, Akiko Kitanou, Christopher J. Walker, Wataru Yashiro, Kazushi Miki, Shusaku Akiba, Akihiko Matsuoka, Makoto Harasawa, and Mamoru Yoshimoto. A charge-ordered spin-dimerized insulator, in which the Ir$^{4+}$ ions form a sublattice of dimer-arrays, has been discovered in Cu$\text{Ir}_2\text{S}_4$. This extraordinary arrangement represents an increase in complexity with respect to other known charge-ordered structures. Other unique states appear in this compound under exposure to x-ray radiation. In the pure material, x-rays induce a persistent structural transition into a dimerized dimer-liquid state, in which the dimers are confined in certain planes in the crystal structure. The x-ray-induced state exhibits short-range incommensurate correlations. Interestingly, no incommensurate state is known to exist in the phase diagram of either pure or doped Cu$\text{Ir}_2\text{S}_4$. X-rays, therefore, produce an entirely new state in this material. The incommensurate correlations reflect the electronic and lattice effects that are supported in the long-range ordered virgin state. A different type of an x-ray-induced transition occurs in Zn-doped Cu$\text{Ir}_2\text{S}_4$. This material consists of a fine mixture of a cubic and a tetragonal phases. X-rays induce a structural transition in which one of these phases is converted into another. For certain Zn concentrations, this transition proceeds in different directions at different temperatures. This is a unique observation, as x-ray-induced transitions usually proceed only in one direction towards a more symmetric state. These experiments show that x-ray radiation does not always lead to a destruction of a certain order in the system. Instead, it can provide a new experimental tool which can be used to drive a metastable system towards an equilibrium state, or even to produce novel states not obtainable by other means.

11:00 AM **Q6.7**

Frustration X-ray Microscopy for Study of Medium-Range

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University of Massachusetts, Amherst, Massachusetts.
Many X-ray techniques exist to probe long- and short-range order in matter, in real space by imaging and in reciprocal space by diffraction and scattering. However, measuring medium-range order in disordered materials is a long-standing problem. Based on fluctuation electron microscopy, which was applied successfully to the understanding of medium-range-order in amorphous materials, we have developed fluctuation x-ray microscopy (FXM). This novel approach offers quantitative insight into medium-range correlations in materials at nanometer and larger length scales. The FXM examines spatially resolved speckle patterns from coherent microdiffraction. The speckle variance depends on higher order correlation functions that are more sensitive to medium-range order. Systematically measuring speckle variance as a function of scattering vector and x-ray illumination size produces a fluctuation map that contains information about the degree of medium-range order and the correlation length. This approach can be used for the exploration of medium-range order and the subtle spatial structural changes in a phenomena under non-equilibrium conditions. These experiments will help us to understand the mechanisms of order-disorder transition and may lead to control of ordering, which is important in developing clusters. The small angle scattering profile, although broad in contrast to selected area electron diffraction which measures a single, presumably straight rope. Using x-ray scattering and a 2-D detector, we show that the alignment of nanotubes in fibers/films is easily and accurately quantified. We find that the degree of nanotube alignment varies significantly with synthesis methods and parameters. The best-aligned fibers span from super-acid suspensions exhibit mosaic spread as narrow as 31°. 26 Tesla-aligned films exhibit an out-of-plane mosaic of 27° and contain the best values reported for nanotube films. X-ray scattering is also used to study C60 filled single-walled carbon nanotube (fullerene peapod) film, which has no in-plane preferred orientation. Here, the finite out-of-plane mosaic enables quantitative measurement of one-dimensional diffraction (chains of C60 pens) from the 2-D rope lattice diffraction for the first time using x-ray scattering. In collaboration with Smalley group (Rice Univ.) and H. Kataura (Tokyo Metropolitan Univ.)

1:45 AM Q6.10 Characterization of 2-dimensional CoPt3 Overlayers With Grazing Incidence Small Angle X-Ray Scattering and Electron Microscopy. Jan Ingo Flige1, Thomas Schmidt1, Roland Kroeger1, Igor Randjelovic2, Vesna Aleksandrovic2, Gabriela Alexe1, Torben Clausen1, Sigrid Bernstorff1, Horst Weller2 and Jens Falta3; 1Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; 3Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

The preparation and investigation of ordered arrays of nanoparticles has attracted a tremendously increasing interest in the last years due to their wide range of potential applications e. g. in opto-electronics, magnetic storage devices and catalysis. In this respect, the concept of efficient two-dimensional self-assembly of colloidal quantum dot with well-controlled access to their wide range of potential applications was a very promising route. In this paper, we present a detailed investigation of the structure and morphology of ordered metallic CoPt3 nanoparticle films adsorbed on various supports using Langmuir-Blodgett techniques. The CoPt3 particles were synthesized via the simultaneous reduction of Pt(II) and thermal decomposition of Co3(CO)2 in a high-boiling coordinating solvent mixture of hexadecylamine-diphenyl ether. After the redissolution of the nanocrystal precipitate in a non-polar solvent the colloids were deposited using a commercial Langmuir trough. Grazing incidence small x-ray scattering (GISAXS) experiments were performed at the SAXS beamline 5.2L at the third-generation synchrotron light source ELETTRA (Italy) using a 8 keV photon energy. An ADG camera allowed the efficient detection of two-dimensional diffuse scattering data as induced by the nanoparticle overlayer. From this, precise information regarding the short-range and long-range order, the particle size distribution and the mean interparticle distance are deduced. Likewise, details of the interrelation between the particle shape and their corresponding lateral arrangement can be inferred from the azimuthal dependence of the diffuse scattering features associated with the quantum dots. As a complementary approach, high-resolution scattering electron microscopy (SEM) images were obtained to map the local superstructure as well as the mesoscopic film morphology. Additionally, transmission electron microscopy (TEM) data will be presented revealing the inner atomic structure of the nanoparticle.

SESSION Q7: X-ray and Neutron Investigations of Microstructure and Strain

Chair: Surita Bhatia
Wednesday Afternoon, December 1, 2004


The increased brilliance of synchrotron x-ray sources and the availability of precise microfocus x-ray optics have enabled recent advances in x-ray microscopy techniques. In particular, we have


Partially aligned single-walled carbon nanotube fibers and films possess many interesting and anisotropic properties. Fibers extruded from suspension exhibit preferred orientation along their axes. In the case of films deposited from suspension onto filter membranes, or by drop casting, the nanotube axes lie preferentially in the film plane. Furthermore, nanotubes can be partially oriented within the plane by depositing films in strong magnetic fields. X-ray scattering data from these macroscopic structures gives the appropriate powder average over many partially-aligned ropes. It thus provides information on macroscopic nanotube alignment, as well as the crystal structure of the two-dimensional rope lattice. We will also help us to understand the mechanisms of order-disorder transition and may lead to control of ordering, which is important in developing clusters. We have recently developed tailored for particular applications. The FXM theory and data analysis technique will be discussed in this paper. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

11:35 AM Q6.8 In-situ Synchrotron Studies of the Multiscale Phase Transformation Behaviors in Bulk Metallic Glass. Xun-Li Wang1,2, Fei Zhou1, Alexandre D. Stoica1, Ling Yang3,4, C. T. Liu1,4, J. D. Almer4 and Wallace D. Porter2; 1Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; 4Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

Scattering instruments with the ability to simultaneously measure diffraction and small angle scattering data provide a unique tool to study materials physics over multi length scales. In-situ, time-resolved measurements allow us to probe the kinetics of the multiscalar phenomena under non-equilibrium conditions. These experiments will play an important role in our understanding of the development of nanostructures. Indeed, several instruments under construction at the Spallation Neutron Source are designed with this foresight in mind. We have recently demonstrated simultaneous wide-angle diffraction and small-angle scattering data using a high-energy synchrotron beamline at the Advanced Photon Source [1]. High-energy X-rays, as well as neutrons, are highly-penetrating, ensuring that the probing volume is representative of the bulk. The data as induced by the nanoparticle overlayer. From this, precise information regarding the short-range and long-range order, the particle size distribution and the mean interparticle distance are deduced. Likewise, details of the interrelation between the particle shape and their corresponding lateral arrangement can be inferred from the azimuthal dependence of the diffuse scattering features associated with the quantum dots. As a complementary approach, high-resolution scattering electron microscopy (SEM) images were obtained to map the local superstructure as well as the mesoscopic film morphology. Additionally, transmission electron microscopy (TEM) data will be presented revealing the inner atomic structure of the nanoparticle.
developed a scanning, polychromatic x-ray scattering technique with submicron spatial resolution on the UNICAT beamline (sector 34) at the Advanced Light Source. In this technique, undulator radiation (8-20 keV) is focused to submicron diameter using elliptical Kirkpatrick-Baez mirrors. Laue diffraction patterns scattered from the sample are collected with a CCD area detector and then analyzed to obtain local crystallographic orientation, strain, and the strain tensor. These microdiffraction capabilities have enabled both 2D and 3D structural studies on mesoscopic length-scales of tenths-to-hundreds of microns. For thin samples such as deposited films, full 3D structural maps are obtained by step-scanning the area of interest. For example, 2D microscopy has been applied in studies of the epitaxial growth of oxide films. For bulk samples, a 3D differential-aperture x-ray structural microscopy (DAXM) technique has been developed that yields the full diffraction information from each submicron volume element. The capabilities of 3D x-ray microscopy have been demonstrated with measurements of intra- and inter-granular orientations and grain boundary motion in polycrystalline Inconel 718 during 3D thermal grain growth. This capability provides the previously lacking, direct link between the experimentally measured 3D microstructural evolution and the results of theory and modeling of materials processes on mesoscopic length scales. *Research supported by the DOE Office of Science, DMS under contract with ORNL, managed by UT-Battelle, LLC; APS is supported by the DOE, Office of Science, BES; UNICAT is supported by UIUC, ORNL, NIST and UOP Res., Inc.

1:45 PM Q7.2
X-ray Microdiffraction Characterization of Deformation Heterogeneities in BCC Crystals. Karen Magid,1, 2, T E. Lillio
dden,3 N. Tamura,1 J. Florando,1 D. Lasila,1 R. Barbash3 and J. W. McMillan1
1 Department of Materials Science and Engineering, University of California-Berkeley, Berkeley, California; 2Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California; 3Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, California.

Deformation behavior of BCC metals is being investigated by x-ray microdiffraction measurements for the purpose of characterizing the dislocation structure that results from uniaxial compression experiments. White beam x-ray microdiffraction studies have been done in order to quantify the density of dislocation core configurations and the growth of single slip in carefully oriented samples. The high brilliance synchrotron source at the Advanced Light Source (Lawrence Berkeley National Lab) and the micron resolution of the focusing optics allow for the mapping of Laue diffraction patterns across a sample. These measurements are then analyzed in order to map the distribution of residual stresses in the crystal. An important finding is the observation of Laue spot "streaking," which indicates localized rotations in the lattice. These may represent an accumulation of same-sign dislocations (so-called geometrically necessary dislocations). Theoretical modeling of the diffraction response for various slip systems is proposed and compared to experimental data. Preliminary results include orientation maps from a highly strained Ti bicrystal and a less highly strained Mo single crystal. The orientation maps of the bicrystal indicate a cell-like structure of dense dislocation walls. This deformation behavior is consistent with previous OIM studies of the same crystal. The results are being used as a proof-of-principle test to understand the more complicated dislocation structures of the Mo single crystals.

2:00 PM Q7.3
In situ Neutron Diffraction Studies of Carbide-Matrix Interactions of Haynes® 230® Nickel Based Superalloy. Tarik A. Salih,1, 3 Bjorn Clausen,2 Hahn Choo1, 2 and Donald W. Brown2
1 Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 2Los Alamos National Laboratory, Los Alamos, New Mexico; 3Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Haynes 230 is a solid solution strengthened, face centered cubic (FCC), nickel based superalloy, with a small percentage of semi-coherent FCC carbides. This semi-coherent nature has led to a compression-anomaly revealed in the behavior of different crystallographic directions under in situ loading. This is thought to be due to the interaction of the carbides and the matrix. In situ neutron loading studies can reveal residual strains and load sharing between two phases in a material. Neutron diffraction experiments were performed at the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at the Los Alamos Neutron Science Center (LANSCE) in order to study the interaction of the carbides with the matrix of the material. Both high and low temperature tension and compression tests were conducted as well as ambient temperature fatigue tests. Although the volume percentage is small (1-3%), the carbides had a significant effect on the mechanical performance. In particular, the creep behavior was compared to the tension and compression tests, the carbides began load sharing at the macroscopic yield point. After this point the bulk of the internal elastic strain was carried in the carbide phase. Upon unloading, the residual strains in the carbide phase were an order of magnitude greater than in the matrix. Theoretical modeling to predict the load-sharing behavior of carbides will be attempted. The present work is supported by the National Science Foundation (NSF), the Interdisciplinary Graduate Education and Research Training (IGERT) Program, under DGE-0918758, and the International Materials Institute (IMI) Program under DMR-0931320, and the Combined Research-Curriculum Development (CRCD) Program, under ECC-0527527 and EEC-0221415, with Drs. P. W. Jennings, L. S. Goldberg, L. Clesceri, C. Huber and Ms. M. Poats as contract monitors.

2:30 PM Q7.5
Probing Mesoscopic Strain Evolution during Creep Deformation: An In-Situ Neutron Diffraction Study. Hahn Choo1, 2, Donald W. Brown3 and Mark A. Bourke1
1Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 2Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Materials Science and Engineering, University of California-Berkeley, Berkeley, California.

The evolution of texture and strain was studied using in-situ time-of-flight neutron diffraction during creep deformation of an austenitic 316FR stainless steel at 180, 240, and 300MPa at 873K (a power-law creep regime) with time resolutions ranging from 120s to 900s. The macroscopic (global) and mesoscopic (lattice) strains were measured simultaneously during creep using extensometer and neutron diffraction, respectively. The SMARTS beamline at the Los Alamos Neutron Science Center. The hil-specific lattice strains were measured to gain insights into the plastic anisotropy at various stages of creep deformation (i.e., primary, secondary, and tertiary regimes). Furthermore, the creep-induced lattice strain behavior was compared to the result obtained from a quasi-static tension test at 873K to understand the implications of the different deformation mechanisms (slip, dislocation creep, or grain-boundary sliding) on the mesoscopic behavior. The results show that the lattice strain evolution during the primary and secondary creep (dislocation creep) is quite similar to the quasi-static case (slip). However, in the tertiary creep regime, the creep-induced lattice strain accommodation is much smaller than the quasi-static case at a given total strain, especially in the (220) reflection. This can be attributed to the grain-boundary sliding facilitated by the grain boundary, leading to a lower strain rate during the creep compared to the quasi-static testing.
Stress-induced martensitic phase transformation and stress-induced twin re-orientation are mechanistically very similar and are central to the pseudo-elastic and thermo-elastic shape memory effects which are beginning to find increased application in modern technology. Because of their high ductility and the capability to be utilized at aplication neutron sources, TOF neutron diffraction is uniquely suited to study both of these deformation processes. We have completed in-situ neutron diffraction loading studies of two shape memory alloys, with NiTi and CuZnAl, using the SMARTS and HIPPO diffractometers at the Los Alamos Neutron Science Center. The technique affords information about the deformed and/or twinned volume fraction as a function of deformation, dislocation density and phase orientations. For instance, a general result is that newly formed martensite tends to support more than its share of load applied subsequent to its formation.

3:30 PM Q7.7 Measurement of Residual Strains with High Depth Resolution by Energy-Variable Diffraction on Synchrotron Beam Lines. Emili Zolotoyabko1, A. Pokryy1, and John Quintana2; 1Materials Science & Engineering, Technion, Haifa, Israel; 2DND-CAT Synchrotron Research Center, Northwestern University, Argonne, Illinois.

Characterization of the microstructure of materials with high spatial resolution is of great interest in the field of nano-science and nano-technology. Achieving high depth resolution in x-ray diffraction measurements is still a problem since x-rays interact much weaker with materials, as compared to electrons, and their penetration depths are limited to a few micrometers. In order to overcome this problem we are developing novel x-ray diffraction technique for synchrotron beam lines, which is energy-variable diffraction (EVD) [1,2]. An idea behind this method is the possibility to precisely change an energy of synchrotron radiation by computer-controlled double-crystal monochromator and, thus, to control accurately the x-ray penetration depth. When increasing energy, the diffraction signal is coming from progressively deeper layers, which allows extracting structural and microstructural information with high depth resolution. Previously by using this method, we demonstrated depth-dependent lamellar size and micro strain fluctuations in seashells [2,3]. This paper is focused on depth-resolved strain measurements in inhomogeneous polycrystalline structures. We show that strain investigation with depth resolution requires detailed analysis of x-ray trajectories, which takes into account the instrument misalignment, change of the height of an incident x-ray beam with energy, and variable penetration of x-rays into the sample depth. This problem can be solved analytically, which yields analytic expression of the diffraction profile measured by EVD. It is shown that the maximum diffraction intensity registered in the detector, is coming from certain depth, which is energy-dependent. This finding opens a way for strain measurements with high depth resolution by changing the x-ray energy in small enough steps. Experimental examples of residual strain measurements across and within lamellar structures demonstrate that homogeneous layers from nature (seashells) demonstrate the capabilities of the method.

3:45 PM Q7.8 Evolution of Polar and Dipolar Dislocation Density from Polychromatic Microdiffraction. Gene Ice and Rozaliya I. Barabash; Metals and Ceramics Div., Oak Ridge National Laboratory, Oak Ridge TN, Tennessee.

Polychromatic diffraction is sensitive to the density and organization of the dislocations, which occurs at several structural levels. At the lowest level structurally stored (dipolar) individual dislocations can exist within a crystal. At a higher structural level dislocations can organize into strongly correlated arrangements including walls and sub-boundaries. After some kind of plastic deformation geometrically necessary (polar) dislocations as well as geometrically necessary boundaries may be formed in a crystal. These cause not only random deformation, but strongly correlated lateral rotation entwined with the crystal, grain, or subgrain. Non homogenous plastic deformation is observed even in single crystals at smaller scale. Density of geometrically necessary dislocations locally oscillates. The wavelength of oscillation is proportional to the total macroscopic deformation. Dislocations spread the conditions for x-ray (or neutron) diffraction transverse to the reciprocal vector of each reflection. Diffraction intensity depends on the second rank dislocation density tensor. The geometrically necessary dislocations density is related to the incompatibility of the plastic deformation and to the lattice curvature. Experimental patterns are therefore sensitive to the ratio between statistically stored and geometrically necessary dislocations. The co-evolution of the statistically stored (dipolar) and geometrically necessary dislocations (polar) may be analyzed, and the ratio between their densities may be obtained from the analysis of the Laue spots intensity distribution. Polychromatic microdiffraction analysis of several examples of dislocation density oscillations in 2D and 3D systems are discussed.

4:00 PM Q7.9 Microstructure of Cross-Hatch Patterns in p/p+ Si (001) by White Beam Diffraction Microscopy and X-ray Micro-Topography. Robert J. B. McBee1, A. P. Zurenko2, and Y. P. Barinov2; 1School of Physics, University of New South Wales, Sydney, Sydney, Australia; 2School of Physics, University of New South Wales, Sydney, Sydney, Australia.

We use the misfit dislocation (MD) nucleation and the dislocation morphology in lightly boron-doped Si epilayers (200 nm) on highly boron-doped (001) wafer (0.015 cm) to study the nucleation and growth of cross-hatch patterns. The misfit dislocations grow to the wafer edge and proceed to the center. Interestingly a dislocation slip-band morphology together with an orthogonal array of type dislocations is able to be observed by synchrotron X-ray diffraction (XRD). The strain-relaxing MDs start to nucleate from the wafer edge and proceed to the center. The morphology of the dislocations consist of two parts: the misoriented dislocation slip-bands are misoriented each other as measured by XRD. The nucleation gradually increases with approaching to the wafer edge. The existence of lattice misorientation is also confirmed by black-and-white dislocation contrast in x-ray topography. These results indicate that the formation of cross-hatch patterns in p/p+ Si is caused by multiplication mechanism in MD nucleation, eventually enabling the strain field of MDs to extend to the top surface of the epilayer.


Interpenetrating Al2O3/Al composites were created by liquid metal infiltration of alumina structures with three-dimensional periodicity produced by a robotic deposition method. Volume-averaged lattice strains in the alumina phase were measured by synchrotron X-ray diffraction at various uniaxial compression stresses up to 350 MPa. Load transfer was observed to occur from the aluminum to the alumina phase, and the average state of stress in the alumina is close to uniaxial compression. Spatially resolved measurements showed variations in load transfer at different positions within the plastic, and damage regions of composite deformation. Using synchrotron X-ray radiography, the extent of damage within the composites was observed. Results are compared with finite element models.

4:30 PM Q7.11 Strain Field under the SiO2/Si(001) Interface Revealed by the Phase-Sensitive X-ray Diffraction Technique. Wataru Yasuhara1,2, Kazuaki Miki1,2, Kazuhiro Sumitani1,2, Toshio Takahashi1, Yoshitaka Yoda3, Kennesuke Takahashi3 and Taeke Hattori3; 1Nanomaterials Laboratory (NML), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan; 2Nanotechnology Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; 3Institute for Solid State Physics (ISSP), University of Tokyo, Chiba, Japan; 4Japan Sychrotron Radiation Research Institute (JASRI), Miki-cho, Sayo-gun, Hyogo, Japan; 5Musashi Institute of Technology, Setagaya-ku, Tokyo, Japan.

Strain near an interface affects its electronic structure, but a full understanding of such strains is still lacking even in the case of SiO2/Si, which has been applied to electronic devices since 1960s. We have developed a new technique, the phase-sensitive X-ray diffraction (PSXD) technique, which is a powerful way to characterize strain...
fields near crystal surfaces, and applied it to a Si(001) wafer whose surface is covered with a thermal oxide layer. It was revealed that there is a small strain field distributing over mesoscopic-range depth (up to several hundred of nm) under the SiO$_2$/Si interface and having a static fluctuation in lateral direction. The PSXD technique is an application of a phenomenon, modulation of the intensity of the crystal-truncation-rod (CTR) scattering under an excitation of a Bragg reflection [1-3], which is an interaction between a two-dimensionally diffracted wave (CTR scattering) and a three-dimensionally diffracted (Bragg reflection) wave. An example will be demonstrated in the case of a Si(001) wafer covered with a thermal oxide layer. The experiment was carried out at BL09XU in SPring-8 in Japan. It was shown that the modulation profile can be characterized by two parameters: the phase shift, which represents the dip or peak position of the modulation profile, and the visibility. Both the phase shift and visibility obtained experimentally were different from those of an ideal perfect crystal. An illustration of the strain field under the SiO$_2$/Si(001) interface which can explain the experimentally obtained modulation profile will be shown. The phase shift can be simply interpreted into the sum of displacements of atomic planes under the interface projected onto the direction perpendicular to the 004 plane (0.16 Å in the case of the example). On the other hand, the visibility indicates that the total displacement has a static fluctuation of at least ±0.13 Å in the direction parallel to the interface. The features revealed by the PSXD technique are expected to provide a new window to understand the oxidation mechanism of Si surface. References [1] W. Yashiro, K. Sumitani, T. Takahashi, Y. Yoda, and K. Miki, Surf. Sci. 550 93 (2004). [2] T. Takahashi and S. Nakata, Surf. Sci. 326 347 (1995); [3] W. Yashiro, K. Sumitani, Y. Yoda, and T. Takahashi, Jpn. J. Appl. Phys. 42 6658 (2003), and references therein.

4:45 PM Q7.12

Microscopic View on Grain Nucleation and Growth Kinetics During Solidification of Aluminum Alloys. Naveed Iqbal$^1$, N. H. van Dijk$^1$, S. E. Offerman$^{1,2}$, M. Moret$^3$, L. Katgerman$^3$ and G. J. Kearley$^1$.$^1$NM, Interfaculty Reactor Institute, TU Delft, Delft, Netherlands; $^2$Materials Science/ID11, ESRF, Grenoble, France; $^3$Laboratory for Materials Science, TU Delft, Delft, Netherlands.

The kinetics of nucleation process during solidification of aluminium alloys plays a vital role in improving mechanical properties of these alloys and can significantly be altered by the addition of micron size intermetallic particles (e.g. TiB$_2$, TiAl$_3$). These particles can act as substrates for heterogeneous nucleation, which causes significant refinement of the final grain size. There is great interest in the quantitative investigation of nucleation kinetics of solid aluminium grains and their growth, with and without added grain refiners. In the present experiment, we have used hard x-rays (70 keV) at beam line ID11 at European Synchrotron Radiation Facility (ESRF), as a tool to obtain in-situ bulk information on the nucleation kinetics during solidification of aluminium alloys containing solute titanium and TiB$_2$ particles, separately and together. The role played by TiB$_2$ particles with and without solute titanium, during the nucleation of the solid phase at a constant cooling rate is quantified through a comparison of results from different samples. This experiment has enabled us to measure the time dependent nucleation of aluminum grains for first time. The experimental results evidence that with the addition of solute titanium to the system of aluminium with TiB$_2$ particles, the nucleation process is enhanced to the extent that the total number of observed nucleated grains is doubled compared to that without titanium solute. The nucleation rate strongly decreases with time and nucleation process is finished for solid fraction below 20%. In addition, it is observed that increase in nucleation process is accompanied by the formation of TiAl$_3$ phase that nucleates before the solidification of aluminium starts. It is proposed that in the presence of solute titanium, TiB$_2$ particles cause the TiAl$_3$ phase to nucleate, that eventually leads to the nucleation of aluminium grains. At the same time, the time dependence of solid fraction during solidification shows also that the segregation of solute titanium in early solidification, reduces the grain growth significantly, that provides enough time for the nucleation sites to activate nucleation in rest of the liquid. The nucleation probability of aluminium grains is found to increase for higher cooling rates. The observed growth curves of the newly formed aluminium grains confirm the parabolic growth in the presence of solute titanium. This new insight about the mechanisms involved in nucleation and growth of individual grains contribute to the development of materials with improved microstructure and better mechanical properties.