

SYMPOSIUM Q

Neutron and X-Ray Scattering as Probes of Multiscale Phenomena

November 29 - December 1, 2004

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* Invited paper

8:30 AM Q1.1

Application of High Energy X-rays to Quantitative Measurements of Volumes of Reciprocal Space: Superstructure and Charge Ordering in NdBaCo₂O₅.

Peter Chupas¹, Stephan Rosenkranz¹, Raymond Osborn¹, 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 systems, 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 volumes of reciprocal space to be collected 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 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 these measurements as it eliminates the need for absorption corrections, which would otherwise rely on variables as tenuous as sample shape, and furthermore, 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 NdBaCo₂O₅.

8:45 AM Q1.2

Temperature Dependent Dynamic Pair Correlations in Relaxor Ferroelectric from Inelastic Neutron Scattering.

Wojciech Dmowski¹, Takeshi Egami^{1,2}, I. K. Jeong³, R. H. Heffner³, J. S. Park⁴, K. S. Hong⁴, M. Hehlen⁵ and F. Trouw³; ¹Univ. Tennessee, Dougherty Engr. Bldg., Tennessee; ²Dept. Physics, U. Tennessee, Oak Ridge Nat. Lab., Knoxville, Oak Ridge, Tennessee; ³Los Alamos Nat. Lab., Los Alamos, New Mexico; ⁴Seoul National Univ., Seoul, South Korea; ⁵LANSCE, Los Alamos Nat. Lab., Los Alamos, New Mexico.

Relaxor ferroelectric oxides, such as Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN), show a diffuse maximum of dielectric susceptibility at the freezing temperature. Susceptibility peak is frequency dependent with a broad relaxation spectrum. This diffuse transition is ascribed to the presence of local polar domains above formal T_c, as evidenced by optical refractive index and Raman intensities, but the detailed microscopic origin is yet to be fully understood. The local ferroelectric polarization persists well above T_c and disappears at the so called Burns' temperature about 630 K. We have measured dynamic structure factor S(Q,ω) for PMN at three temperatures, in the proximity of Burns' temperature, at room temperature and at 40K. It is observed that in the energy range 10-35 meV that dynamic structure factor exhibits much more "structure" at high temperature than at the low one. This observation we ascribe to the "motion narrowing" when oxygen dynamics becomes decoupled from the lead and the local symmetry of Pb atoms become cubic. Furthermore we analyze data 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 time-of-flight diffraction experiment to reveal important differences in the structure at different temperatures. The most obvious changes appear in the range of 2.4-3.2 Å. Most of the changes involve short and long bonds between Pb and oxygen atoms and indicate that dynamic off-centering of Pb disappears at the Burns' temperature.

9:00 AM *Q1.3

Revisiting the ground state of an insulating, half-doped manganite with soft x-ray resonant diffraction.

Jessica Thomas¹, John Hill¹, Stephane Grenier¹, Peter Abbamonte¹ and Michel van Veenendaal^{2,3}; ¹Brookhaven National Laboratory, Upton, New York; ²Northern Illinois University, Dekalb, Illinois; ³Argonne National Laboratory, Argonne, Illinois.

X-ray and neutron diffraction experiments support a picture of charge and orbital order of 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 T_{CO}. The Mn³⁺ sites are Jahn-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-orbital order transition temperature. However, the dynamics which lead to this particular ordering are still not well 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 is complete remains a controversial issue. Resonant x-ray scattering near the atomic Mn L_{II,III} absorption edges (2p → 3d) is a powerful probe for studying orbital and spin correlations in manganites. At the Mn L-edges (~650 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 diffraction measurements at the Mn L-edges which allowed a direct comparison of orbital and spin correlations in the near-half doped manganite Pr_{0.6}Ca_{0.4}MnO₃. Comparing the widths of the magnetic, Q = (1/2, 0, 0), and orbital, Q = (0, 1/2, 0), diffraction peaks, we found that the magnetic correlation length exceeded that of the orbital order 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 odds with the conventional CE, ionic picture in which only the Mn³⁺ 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 Peral², Thomas Proffen³ 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 still do not help solve many problems associated with understanding diffusion and the catalytic and adsorptive properties of zeolites, mainly because the need of 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 layer of pores that is stacked differently in the c direction. This layer is extended infinitely in a and b and has a height of approximately 7 Å along the c direction. Thus, the structure of both polytypes were refined using neutron and synchrotron data up to 7 Å. 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 refinements show that the PDF method is a viable technique 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 most contracting materials known, using a synchrotron PDF at room temperature and at 753K. 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.

9:45 AM Q1.5

Pair Distribution Function Analyses of Structural Relaxation in a Zr-Based Bulk-Metallic Glass. Mark L. Morrison¹, Wojciech Dmowski¹, Peter K. Liaw¹, C. T. Liu², Jim W. Richardson³, Evan R. Maxey³, Raymond A. Buchanan¹, Tim Wilson¹, Cang Fan¹, Hahn Choo¹, Takeshi Egami¹ and Wallace D. Porter²; ¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois.

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 crystalline phase 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 systems that can form massive (bulk) glassy 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 $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10.0}Ti_{5.0}$ (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 (NSLS) 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 $La_{1.8}Sr_{0.2}NiO_4$. L. Hao Tjeng¹, Christian Schuessler-Langeheine¹, Justina Schlappa¹, Zhiwei Hu¹, Maurits W. Haverkort¹, Mohammed Benomar¹, Oliver Friedt¹, Markus Braden¹, Arata Tanaka², Enrico Schierle³, Holger Ott^{1,3}, Eugen Weschke³, Guenter Kaindl³, George A. Sawatzky⁴, Adrivo Rusydi⁵ and Peter Abbamonte⁵; ¹II. Physikalisches Institut, Universitaet zu Koeln, Koeln, Germany; ²ADSM, Hiroshima University, Hiroshima, Japan; ³Institut fuer Experimentalphysik, Freie Universitaet Berlin, Berlin, Germany; ⁴Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada; ⁵NSLS, Brookhaven National Laboratory, Upton, New York.

We report about the direct observation of charge order in Sr-doped La_2NiO_4 using resonant soft x-ray diffraction at the Ni $L_{2,3}$ 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 $La_{1.8}Sr_{0.2}NiO_4$ 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 from the same sample, because the comparably short penetration depth of soft x-rays together with the availability of well focused 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, Sujoy Chakravarty², T. Gutberlet¹, H.-C. Wille³, O. Leupold³ and R. Rueffer³; ¹Laboratory for Neutron Scattering, Paul Scherrer Institute, Villigen PSI, AG, Switzerland; ²Inter University Consortium 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. However, 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 $FeZr/^{57}FeZr$ multilayers. It has been shown that both the techniques are complementary to each other and give 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

Structure and dynamics of water adsorbed in carbon nanotubes: A joint neutron-scattering and molecular-dynamics study. Nicolas R. de Souza¹, Alexander I. Kolesnikov¹, Chun K. Loong¹, Alexander P. Moravsky², Raouf O. Loutfy² and Christian J. Burnham³; ¹Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois; ²MER Corporation, Tucson, Arizona; ³Henry Eyring Center for Theoretical Chemistry, University of Utah, Salt Lake City, Utah.

The advent of nanocarbons, from single- and multiple-walled nanotubes to nanohorns, avails model studies 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 nanotubes and the weak interaction between 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 nanotube-confined water/ice. This configuration results in a hydrogen-bond connectivity that markedly differs from that in bulk water. This significantly softened hydrogen-bond network manifests in strong energy shifts of the observed and simulated inter- and intra-molecular vibrations. The very 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.

Lumsden²; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Condensed Matter Sciences 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, $La_4Ru_2O_{10}$, provides a particularly good example. The structure comprises corner-shared RuO_6 octahedra forming corrugated planes. At 160K, it undergoes 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 $4d_4 t_{2g}$ electrons. The magnetic susceptibility collapses suddenly 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 strong spin fluctuations within the $S=1$ ground state. Below the transition, a spin

gap of over 40 meV develops. Single crystal measurements using the the MAPS spectrometer (ISIS Pulsed Neutron Facility) reveal very weak dispersion of this excitation, but a very strong modulation of the intensity with Q. We will discuss two possible models; either the change in orbital configuration induces local singlets, which are coupled by interionic exchange, or the singlets are themselves formed by a strong dimerization of neighboring ion spins. 1. P. Khalifah, R. Osborn, Q. Huang, H. W. Zandbergen, R. Jin, Y. Liu, D. Mandrus, R. J. Cava, Science 297, 2237 (2002) This work was supported by the US DOE, Office of Science, under contracts W-31-109-ENG-38 and DE-AC05-00OR22725.

SESSION Q2: Neutron and X-ray Scattering for
Material Dynamics and Polymer/Biopolymer Structure
Chair: Darrin Pochan
Monday Afternoon, November 29, 2004
Hampton (Sheraton)

1:30 PM Q2.1

Structure and Dynamics of Propylene Oxide and Trimethylene Oxide Clathrate Hydrates. Inmaculada Peral^{1,2} and Camille Y. Jones¹; ¹NIST, Gaithersburg, Maryland; ²University of Maryland, College Park, Maryland.

Gas hydrates are water-based, natural gas-containing inclusion compounds that occur in nature in vast deposits under the ocean floor and in the arctic permafrost. (1) They belong to a larger family of inclusion compounds known as clathrate hydrates. The structure of a clathrate hydrate (CH) comprises water molecules held together by hydrogen bonds in a three-dimensional "host" network of spherical polyhedra, or cages, which contain a small "guest" molecules. Neutron powder diffraction studies in the range (10-160) K the CH with the guest tetrahydrofuran (C₄H₈O·17²H₂O) have shown that distortions occur in the host as a function of temperature. (2) In particular, distortions at low temperature brings H atoms closer than the O atoms to the inner center of the cage, and indicate that changes in the specific configuration of O and H may be important in the determination of the guest-host interactions and the resulting CH properties. An explanation for the distortions is suggested in the findings from quasielastic neutron scattering studies (QENS) of trimethylene oxide (TMO) CH, (3) chemical formula C₃H₆O·17²H₂O. The QENS results show distinct regions of high-temperature and low-temperature rotational dynamics are observed, and activation energy for guest rotation that is higher in the high-temperature regime than at low temperatures. This presentation describes recent neutron diffraction and QENS results in the range (5-260) K on the CHs of the cyclic ethers THF, TMO, and propylene oxide. A relationship between the structural distortions in the host and the changes in the guest dynamics is proposed. 1. Makagon, Y. F.; Trebin, F. A.; Trofimuk, A. A.; Tsarev, V. P.; Chersky, N. V.; Dokl. Acad. Sci. USSR - Earch Sci. Sect. 1972, 196, 197-200. 2. Jones, C. Y.; Marshall, S. L.; Chakoumakos, B. C.; Rawn, C. J.; Ishii, Y. "Structure and Thermal Expansivity of Tetrahydrofuran Deuterate Determined by Neutron Powder Diffraction". J. Phys. Chem. B 2003, 107(25), 6026-6031. 3. Jones, C. Y.; Peral, I. "Dynamics of Trimethylene Oxide in a Structure II Clathrate Hydrate". Submitted to The American Mineralogist.

1:45 PM Q2.2

Interactions of Hydrating Tricalcium and Dicalcium Silicate by Quasi Elastic Neutron Scattering. Vanessa Kate Peterson¹, Dan A. Neumann² and Richard A. Livingston³; ¹Center for Neutron Research/Department of Materials Science and Engineering, NIST/University of Maryland, Gaithersburg, Maryland; ²Center for Neutron Research, NIST, Gaithersburg, Maryland; ³Federal Highway Administration, McLean, Virginia.

Cement is the most important and widely used building material in the world. Cement clinker is a complex calcium silicate mixture, and is interground with a small amount of gypsum to make cement powder. Cement paste is produced when cement powder is combined with water, where hydration processes take place during which the mixture gains strength. Tricalcium silicate is the primary component of Portland cement clinker, comprising 50-70wt.% of the total composition, and is the component responsible for early strength development in cement paste. Dicalcium silicate is the second most abundant component, comprising 15-30wt.% of clinker. Although dicalcium silicate contributes little to early strength development, by one year its strength is comparable to that of tricalcium silicate paste. Although there exist numerous studies on the separate hydration of tricalcium silicate and dicalcium silicate, almost no studies on their interaction have been made, and it is the complex interaction of these phases that makes cement different from its constituent components. Quasi Elastic Neutron Scattering (QENS) allows the state of the water in hydrating cement paste to be studied in-situ with time.

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 I. Kolesnikov¹, Chun-Keung Loong¹, Alexander P. Moravsky², Raouf O. Loutfy² and Christian J. Burnham³; 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 Å diameter), double-walled carbon nanotubes (DWNT of 25 Å diameter), carbon nano-horns and fullerene-C60 encapsulated into SWNT (so called C60-peapods), aiming at the characterization of the vibrational spectra over a wide energy scale, from collective motions to localized atomic vibrations. The spectrum of nano-horns was similar to that of SWNT, and the latter one agrees with the main features reported in the literature. The INS spectrum of C60-peapods 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-peapods 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 shift to higher energies. 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-BES under 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. Cicerone; 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 preservative 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 similar 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 of slower protein dynamics 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. Alexei Sokolov, Department of Polymer Science, The University of Akron, Akron, Ohio.

Hydrated proteins and DNA demonstrate a dynamic transition at temperatures T_d 200-230K. 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 above T_d. Microscopic nature of the slow process and its relation to protein functions are discussed. We emphasize that T_d observed for hydrated biomolecules (T_d 200-230K) and for proteins placed in glycerol (T_d 270K) coincides well with the temperatures of the dynamic crossover (dynamic arrest) in the pure solvents (is estimated to be TC 220-230K in water [4] and TC 270-290K in glycerol [5]). This observation supports our earlier speculations [1,2] that the dynamic crossover of solvents controls the dynamic transition in biomolecules, i.e. the dynamic arrest 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 importance of translation diffusion of water 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, 7053 (1999). 2. A.P. Sokolov, et al., J.Biological Physics 27, 313 (2001). 3. G. Caliskan, et al., J.Chem.Phys. 121, July 15 issue (2004, in print). 4. A.P. Sokolov, et al., Phys.Rev.B 51, 12865 (1995); R. Torre, et al., Nature 428, 296 (2004). 5. A.P.Sokolov, J.Non-Cryst.Solids 235-237, 190 (1998). 6. M. Tarek, D. Tobias, Phys.Rev.Lett. 88, 138101 (2002). 7. A. L. Tournier, 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 Jyotsana Lal²; 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 crystalline transition at less than 1% wt protein content, 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 method to align nematic F-actin domains, thus the neutron scattering technique is not 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. Gudrun Schmidt¹, Elena Loizou¹, Paul D. Butler² and Lionel Porcar²; 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 clay surfaces are covered. Any excess polymer in solution leads to formation of two interpenetrating phases: network like polymer-clay structures entangled with pure polymer aggregates. We assume that these two phases lead to unusual and unexpected morphology.

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. Zhu³, Amitabh Bansal³, L.S. Schadler³ and L. B. Lurio²; ¹Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois; ²Department of Physics, Northern Illinois University, DeKalb, Illinois; ³Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, New York.

Alumina/polymethylmethacrylate (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 0.1 wt.% of the filler concentration [1]. This phenomenon is accompanied by a brittle-to-ductile transition with a large increase in

the 'strain-to-failure'. In silica/polyvinylacetate nanocomposites it is found that altering the interfacial bonding between the polymer and the particle by subjecting its surface to 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 nano-sized inorganic fillers, we have undertaken small-angle neutron (SANS), and ultra small angle x-ray scattering (USAXS) to probe their structure and X-ray photon correlation spectroscopy (XPCS) to understand their dynamics. SANS and USAXS studies of alumina-PMMA composites show a large degree of aggregation and agglomeration of alumina that depends on the size of the nanoparticles. The size distribution of the nanoparticles is distinctly different across the percolative transition. USAXS data on silica-PVAc nanocomposites show an average aggregation of about 250 angstroms, which is significantly reduced in the case of surface treated fillers. Evidence suggests that the surface fractal dimension, which is a measure of surface roughness, is directly related to reinforcement characteristics of the composite [3]. XPCS measurements apart from revealing a non-brownian like diffusion of the particles, also suggests that the diffusion is faster at higher alumina concentrations. This work benefited from a grant from Office of Naval Research to LS at RPI, and IPNS and APS facilities funded by DOE under contract no. W-31-109-ENG-38 to the University of Chicago. UNICAT facility is supported by the DOE, the State of Illinois-IBHE-HECA, NSF, NIST (U.S. DOC) and UOP LLC. [1]. B.J. Ash, L.S. Schadler, R.W. Siegel, Mater. Lett. 55, 83 (2002); *ibid*, Macromolecules, 37, 1358 (2004). [2]. S.S. Sternstein, and A.J. Zhu, Macromolecules 35, 7262 (2002). [3]. R.A. Narayanan et. al, unpublished.

4:15 PM Q2.9

Thin Polymer Film Structure using Resonant Soft X-ray Contrast Variation. Cynthia Welch¹, Rex Hjelm¹, E.Bruce Orler¹, Debra Wroblewski¹, Marilyn Hawley¹, Joseph Mang¹ and Jeffrey Kortright²; ¹Los Alamos National Laboratory, Los Alamos, New Mexico; ²Lawrence Berkeley National Laboratory, Berkeley, California.

The structure of thin (<1 μm) poly(ester urethane) (PESU) films is analyzed with resonant soft 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 π* and σ* absorptions. The PESUs studied here are segmented copolymers of immiscible hard, aromatic and soft, aliphatic segments. Extensive studies of thick films (≈ 1mm) reveal that, in the bulk material, the segments nano-phase segregate into hard and soft segment-rich domains on the size scale of ca 10 nm. The hard domains act as network cross-links, giving the unique mechanical properties that make PESU thin films excellent materials for coatings, binder, and adhesive applications. Morphological studies of thin PESU films by small-angle scattering (SAS) have proven difficult due to the lack of material in the beam and the weak contrast 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 the 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 features 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 resonance techniques has relied on high-energy x-ray resonances of heavy elements in chemically modified polymers. By extending this method to the lower energy ranges associated with absorption edges of the light atoms, we significantly broaden this technique and enable the characterization 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 Tian^{1,2}, Seery A. P. Thomas^{3,2} and Weiss A. Robert^{1,2}; 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 copolymers composed of either N,N-dimethylacrylamide (DMA) or N-isopropylacrylamide (NIPA) and 2-(N-ethylfluorooctanesulfonamido)ethyl acrylate, FOSA, 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 10 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 successfully performed for those 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 molecular weight 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: Surita Bhatia
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 Ilavsky² and Glen Fox³; ¹Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ²XOR, Argonne National Laboratories, Chicago, Illinois; ³High Density FRAM Development, Ramtron International Corp., Colorado Springs, CO 80921, Maryland.

The (111) fiber texture in 200 nm thin films of Pt deposited by magnetron sputtering on 150 nm (001) Si wafers has been characterized by various diffraction techniques, primarily x-ray. Parallel beam texture 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 FWHM of the texture profile and orientation of the fiber texture axis, was very completely characterized. After cleaving the wafers into ≈10 mm squares, 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 precisions 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, TECSER UMR CNRS 6122, Univ. Paul Cezanne, Marseille Cedex 20, France.

X-ray diffraction was recognized from the early days as very sensitive to 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 mechanics diffraction may thus 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 and powerful methods (anomalous diffraction, coherent diffraction, micro-diffraction). 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 W. Schaefer^{1,3}, Ryan S. Justice¹, Hilmar Koerner², Richard Vaia², Chungui Zhao² and Mingshu Yang²; ¹Chemical and Materials

Engineering, University of Cincinnati, Cincinnati, Ohio; ²MLBP, Air Force Research Laboratory, WPAFB, Ohio; ³Institute of Chemistry, Chinese Academy of Sciences, Beijing, Haidian, China.

In spite of concerted international effort to elucidate the dispersion of layered silicates in solution and solid matrices, there is minimal agreement regarding the large-scale structure of dispersed clays, including even a consistent definition of exfoliated. 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 measurement, however, provides no information on large-scale layer-layer correlations, local fluctuations in layer concentration, orientational correlations and hierarchical morphology. Here we discuss the use of small angle x-ray scattering and light scattering to characterize hierarchical morphology over length scales from 0.5 nm to 50 μm. Over a limited q-range, for fully exfoliated clays in solution, we find power-law dependence of the intensity on q, where q is the magnitude of the scattering vector. The power-law slope of -2 (expected for sheet-like structures), however, is found only for length scales below 10 nm. On larger length scales deviations from -2 imply substantial disorder of the dispersed sheets. Armed with the information from the solutions of various levels of exfoliation, the dispersion of organically modified montmorillonite in polyamide-66 is discussed. The results indicate complete exfoliation with no evidence of sheet-like morphology.

9:30 AM *Q3.4

X-Ray Diffraction as a Probe for Elastic Strain: Micro- and Nanoscale Investigation of Thin Metal Films. Ralph Spolenak, Max Planck Institute for Metals Research, Stuttgart, Germany.

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 in volumes smaller than a cubic micron. A 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 focus on size effects in thin film plasticity and fracture, specifically in Cu and Ta bilayers on polyimide substrates. Future perspectives and frontiers of the techniques will be critically assessed and commented.

10:30 AM *Q3.5

Ultrasmall-Angle X-ray Scattering Studies of Highly Anisotropic Materials. Andrew J. Allen, Materials Science and Engineering Lab., NIST, Gaithersburg, Maryland.

Small-angle scattering of neutrons or x-rays (SANS or SAXS) has become a well established means of determining and quantifying the statistically representative microstructures of heterogeneous materials. The quantitative parameters obtained complement the visual information gained from electron microscopy or tomography. Conventional SANS and SAXS probe the scale regime from nanometers to approximately 0.1 micrometer. Ultrasmall-angle scattering methods, which employ the Bonse-Hart geometry, can 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 slit-smearing, the slit-smearing may be removed by the inclusion of side-reflection crystals before and after the sample. Unsmear USAXS data are then obtainable for any given azimuthal sample orientation, providing the capability for arbitrarily fine anisotropic resolution in the study of highly oriented systems. For example, the effects at all length scales of thermal cycling on the highly anisotropic void microstructures of technologically important electron-beam physical vapor deposits (EB-PVD) have been explored. These issues will be discussed with reference to recent studies using the NIST-built USAXS facility at the UNICAT sector of APS.

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 volumes (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 60 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 electrodeposited 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

Real-Time X-Ray Characterization of Sputter Deposition of Tantalum Films. Sabrina Lin Lee¹, Justin Mueller¹, Mick Cipollo¹ and Greg Vigilanti¹; ¹Benet Labs, US Army Research Development and Engineering Center, Watervliet, New York; ²Benet Labs, US Army Research Development and Engineering Center, Watervliet, New York; ³Benet Labs, US Army Research Development and Engineering Center, Watervliet, New York; ⁴Benet Labs, US Army Research Development and Engineering Center, Watervliet, New York.

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 compliment the in-situ system. Depositions were made on glass, silicon wafer, and A723 steel 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 0.65-13 Pa (5-100mTorr), 10-75 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 target and substrate 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 Rieker¹, Pete Jemain² and Jan Ilavsky²; ¹Div. of Materials Research, National Science Foundation, Arlington, Virginia; ²Argonne National Laboratory, 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.

SESSION Q4: X-rays and Neutrons as Probes of
Electronic and Magnetic Structure
Tuesday Afternoon, November 30, 2004
Hampton (Sheraton)

1:30 PM *Q4.1

The phase-diagram of Ca_{2-x}Sr_xRuO₄: relation between crystal structure and physical properties. Markus Braden¹, Oliver Friedt^{1,2}, Olaf Schumann¹, J. Baier¹, P. Steffens¹, M. Kriener¹, T. Lorenz¹, A. Gukasov², P. Radaelli³, S. Nakatsuji⁴ and Y. Maeno³; ¹Universitaet zu Koeln, II. Physikalisches Institut, Koeln, Germany; ²Laboratoire Leon Brillouin, Gif-sur-Yvette CEDEX, France; ³ISIS Facility, Chilton, Didcot, United Kingdom; ⁴Kyoto University, Kyoto, Japan.

Substituting the Sr in the spin-triplet superconductor by Ca yields an extraordinarily rich phase diagram in view of the fact that these ions differ only in their size. For intermediate Ca concentration one finds the second highest electronic mass ever observed in an oxide as well as meta-magnetism; the end member, Ca₂RuO₄, is an antiferromagnetic Mott-insulator. The distinct phenomena are driven by several structural distortions associated with tilting and rotating of the RuO₆ octahedra. The orbital occupation of the three t_{2g}-levels in these distorted crystal structures is found to be the decisive factor for the physical properties.

2:00 PM Q4.2

Spin-Analyzed Diffuse Reflectometry of Magnetic Thin Films with a Polarized ³He Analyzer. Wangchun Chen^{1,2}, Kevin O'Donovan^{1,3}, Julie Borchers¹, Charles Majkrzak¹ and Thomas Gentile¹; ¹NIST, Gaithersburg, Maryland; ²Indiana University, Bloomington, Indiana; ³University of Maryland, College Park, Maryland.

Patterned magnetic arrays have recently attracted considerable attention due to their technological applications in high density data storage media. Polarized neutron reflectometry (PNR) is a powerful probe that characterizes the magnetization depth profile and magnetic domains in such materials. Most reflectometers use supermirrors that are well-matched for specular PNR. However, complete characterization of the magnetic off-specular scattering requires polarization analysis devices for diffusely reflected neutrons. The currently available supermirror spin analyzers have limited angular acceptance. Polarized ³He gas, produced by optical pumping, can be used to polarize or analyze neutron beams because of the strong spin dependence of the neutron absorption cross section for ³He. ³He spin filters have been identified as important polarizing elements in the development of polarized neutron scattering instruments for the upcoming spallation neutron source (SNS) because they are broadband and suitable for divergent scattered beams. Here we report efficient polarization analysis of diffusely reflected neutrons in a reflectometry geometry using a polarized ³He analyzer in conjunction with a position-sensitive detector (PSD). We obtained spin-analyzed two-dimensional Q_x-Q_z reciprocal space maps for a patterned array of Co antidots in the saturated and the demagnetized states. Data obtained from a ³He analyzer and a PSD were compared with those obtained from a conventional supermirror analyzer, and show good agreement between them. The preliminary results for the upcoming experiments with a ³He analyzer and a PSD using a patterned dot sample and/or a rare-earth alloy exchange spring will also be discussed. Whereas the magnetization depth profile can be obtained from specular PNR, diffuse PNR is needed to obtain information on lateral magnetic domains and magnetic roughness. For these experiments, ³He gas is polarized by the spin-exchange optical pumping (SEOP) method and stored in a uniform magnetic field provided by a shielded solenoid. We address two important issues for achieving the best performance of the ³He spin-analysis device: high ³He polarization and long polarization storage time of the cell. Using a spectrally narrowed diode laser array we have recently achieved ³He polarizations of 74% to 77% in ³He cells ranging from 260 cm³ to 500 cm³ in volume. At 75% ³He polarization, an analyzing efficiency of 0.97 can be obtained with a neutron transmission for the desired spin state of 0.44.

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. Downes², Cormac McGuinness³, Per-Anders Glans¹, Timothy Learmonth¹, Yufeng Zhang¹ and Kevin E. Smith¹; ¹Department of Physics, Boston University, Boston, Massachusetts; ²School of Chemical and Physical Sciences, Victoria University, Wellington, New Zealand; ³Department of Physics, Trinity College Dublin, 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 previously 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 that previously published SXE studies of organic semiconductors 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 determination of the non-ionized electronic structure. Supported in part by the donors of the Petroleum Research Fund, administered by the ACS, and by the NSF under DMR-0304960. Our spectrometer system is funded by the U.S. ARO under DAAD19-01-1-0364 and DAAH04-95-0014. Experiments were performed at the NLS 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).

2:30 PM *Q4.4

Structure and Dynamics of Na_xCoO_2 and the Hydrated Superconductor. Jeff Lynn¹, Q. Huang¹, Robert J. Cava² and Y. S. Lee³; ¹NCNR, NIST, Gaithersburg, Maryland; ²Department of Chemistry and Princeton Materials Institute, Princeton University, Princeton, New Jersey; ³Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The properties of the Na_xCoO_2 class of materials are very interesting from a number of standpoints. It is a triangular lattice of spin-1/2 ions-prototype RVB system-where a high thermoelectric-power Curie-Weiss metallic paramagnet is found for $\text{Na}_{0.7}\text{CoO}_2$, a charge ordered insulator at $x=0.5$, and a paramagnetic metal where superconductivity is induced in $\text{Na}_{0.3}\text{CoO}_2$ when it is intercalated with water. We have used neutron diffraction and inelastic scattering to characterize the crystal structure and lattice dynamics, and relate these to the observed physical properties. The basic structure of Na_xCoO_2 is hexagonal and consists of robust layers of CoO_2 interspersed by Na layers with two inequivalent sites. Two special cases are $x=1$ where one of these sites is fully occupied and the other empty, and $x=1/2$ where both sites have equal occupancies of $1/4$ and the system is a charge ordered insulator. For general x the site occupancies are inequivalent and vary systematically with x . In the regime of $x=0.75$ we find a first-order transition from a high symmetry Na site at low T to a three-fold split site (with lower symmetry) at high T. This transition is first order and varies with x . For the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.4(\text{H}/\text{D})_2\text{O}$ superconductor, the water forms two additional layers between the Na and CoO_2 , increasing the c -axis lattice parameter of the hexagonal $\text{P6}_3/\text{mmc}$ space group from 11.16 Å to 19.5 Å. The Na ions are found to occupy a different configuration from the parent compound, while the water forms a structure that replicates the structure of ice to a good approximation. We find a strong inverse correlation between the CoO_2 layer thickness and the superconducting transition temperature (T_C increases with decreasing thickness). The phonon density-of-states for $\text{Na}_{0.3}\text{CoO}_2$ exhibits distinct acoustic and optic bands, with a high-energy cutoff of 100 meV. The lattice dynamical scattering for the superconductor is dominated by the hydrogen modes, with librational and bending modes that are quite similar to ice, supporting the structural model that the water intercalates and forms ice-like layers in the superconductor. J. W. Lynn, Q. Huang, C. M. Brown, V. L. Miller, M.L. Foo, R.E. Schaak, C. Y. Jones, E. A. Mackey, and R. J. Cava, Phys. Rev. B68, 214516 (2003). Q. Huang, M. L. Foo, J. W. Lynn, H. W. Zandbergen, G. Lawes, Y. Wang, B. Toby, A. P. Ramirez, N. P. Ong, and R. J. Cava, J. Phys.: Cond. Matter (submitted). Q. Huang, M. L. Foo, J. W. Lynn, B. H. Toby, R. A. Pascal, H. W. Zandbergen, and R. J. Cava, Nature Materials (submitted) Q. Huang, B. Khaykovich, F. C. Chou, J. H. Cho, J. W. Lynn, and Y. S. Lee, Phys. Rev. B (submitted). Work at Princeton supported by NSF, DMR 02-44254, and DOE BES, DE-FG02-98-ER45706. Work at MIT supported by NSF MRSEC, DMR 02-13282.

3:30 PM Q4.5

Electronic Structure of the Organic Semiconductor Vanadium Oxide Phthalocyanine (VOPc) measured using High Resolution Resonant Soft X-ray Emission Spectroscopy. Yufeng Zhang, Timothy Learmonth, 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 non-ionizing spectroscopy, the electronic structure 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 an ultra-high vacuum organic molecular beam deposition system, and transferred under vacuum to the spectrometer system on the beamline. As 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 C 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 photons at the V 2p_{3/2} absorption edge. Both dipole forbidden 3d - 3d excitations and O 2p - V 3d charge transfer excitations are observed. The relationship of these excitations to those observed in vanadium oxide crystals will be explored. Supported in part by the donors of the Petroleum Research Fund, administered by the ACS, by the NSF under DMR-0304960. Our spectrometer system 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. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.E. Rubensson, and N. Wassdahl, Rev. Sci. Instrum. 60 (1989) 1690. [2]. S.M. Butorin, D.C. Mancini, J.H. Guo, N. Wassdahl, J. Nordgren, M. Nakazawa, S. Tanaka, T. Uozumi, A. Kotani, et al., Phys. Rev. Lett. 77 (1996) 574. [3]. J.E. Downes, C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390 (2004) 203.

3:45 PM Q4.6

X-ray laser induced photoelectron spectroscopy for single-state measurements. Art J. Nelson¹, Jim Dunn², T. van Buren¹ and Jim Hunter²; ¹CMS MSTD, LLNL, Livermore, California; ²PAT V-Division, LLNL, Livermore, California.

We demonstrate single-shot x-ray laser induced time-of-flight photoelectron spectroscopy on semiconductor and metal surfaces with picosecond time resolution. The LLNL COMET compact tabletop x-ray laser source provides the necessary high photon flux ($>10^{12}$ /pulse), monochromaticity, picosecond pulse duration, and coherence for probing ultrafast changes in the chemical and electronic structure of these materials. Static valence band and shallow core-level photoemission spectra are presented for ambient temperature Ge(100) and polycrystalline Cu foils. Surface contamination was removed by UV ozone cleaning prior to analysis. In addition, the ultrafast nature of this technique lends itself to true single-state measurements of shocked and heated materials. Time-resolved electron time-of-flight 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.

4:00 PM *Q4.7

Novel phases at magnetic quantum phase transitions in metals. Hilbert v. Lohneysen, ¹Institut f. Festkoerperphysik, Forschungszentrum Karlsruhe, Karlsruhe, Germany; ²Physikalisches Institut, Universitaet Karlsruhe, Karlsruhe, Germany.

In a number of metallic systems, long range magnetic order can be tuned to zero temperature by an external parameter such as pressure or chemical composition. At such a quantum phase transition (QPT), the quantum energy of critical fluctuations becomes a relevant energy compared to the thermal energy, leading to novel quantum critical behavior. While QPT's are of interest in their own right, the fact that temperature is the only relevant energy scale gives access to low energy scales otherwise masked by the magnetic order, with the prospect of new physics. We will discuss two examples of possible new phases near a QPT: (i) Highly anisotropic magnetic fluctuations in $\text{CeCu}_{6-x}\text{Au}_x$ observed by inelastic neutron scattering arise when approaching the QPT occurring at $x = 0.1$, despite the fact that long-range incommensurate order for $x \geq 0.15$ is three-dimensional. These fluctuations extend over a rather large concentration range $0 \leq x \leq 0.2$ on either side of the QPT [1]. (ii) MnSi is a particularly clean system where the QPT can be tuned by hydrostatic pressure. The long-wavelength helical magnetic structure (wavelength 180 Å) retains its periodicity when approaching the QPT but loses its orientation, as observed via neutron scattering under pressure [2]. This "partial melting" is reminiscent of orientational order in liquid crystals and presents a truly novel magnetic phase. How this partial order is related to the non-Fermi-liquid behavior observed in electronic transport over an extended pressure and field range [3] has yet to be established. [1] O. Stockert et al., Phys. Rev. Lett. 80, 5627 (1998); H. v. Lohneysen, Acta Phys. Pol. B 34 707 (2003). [2] C. Pfeleiderer et al., Nature 427, 227 (2004). [3] C. Pfeleiderer et al., Nature 414, 427 (2001). *Work done in collaboration with C. Pfeleiderer, L. Pintschovius, D. Reznik and O. Stockert.

4:30 PM *Q4.8

In-situ X-ray Reflectivity Study of Oxidation Kinetics in Iron and Stainless Steel. Do Young Noh¹, Do Hyung Kim¹, Sang Soo Kim¹, Sunhil Sinha² and Keng Liang³; ¹Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea; ²Physics, UCSD, San Diego, California; ³NSRRC, Hsinchu, Taiwan.

Since Cabrera and Mott's pioneering theoretical work on oxidation in metals, oxidation kinetics has been investigated extensively both

experimentally and theoretically. Understanding the oxidation mechanism is important for practical purpose in many cases, since thin oxide films 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-16.31%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 steady-state, we estimate the potential drop at the metal/oxide interface, in the oxide, and at the oxide/solution interface.

4:45 PM *Q4.9 TRANSFERRED TO *Q4.8

SESSION Q5: Poster Session: Neutron and X-Ray
Scattering as Probes of Multiscale Phenomena
Chair: Darrin Pochan
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

Q5.1

Investigation of Buried GaAs/Ge/Si (001) Interfaces using Anomalous X-ray Reflectivity. Eugen Wintersberger¹, Julian

Stangl¹, Tobias Schuelli¹, Mojmir Meduna¹, Guenther Bauer¹, Yves Chriqui², Ludovic Largeau², Isabelle Sagnes², Guillaume Saint-Girons², Daniel Bensahel³, Yves Campidelli³ and Olivier Kermarrec³; ¹Semiconductor physics, Johannes Kepler university, Linz, Austria; ²LPN, CNRS, Marcoussis, France; ³ST Microelectronics, Crolles, France.

We studied the structural properties of GaAs layers which were deposited on Ge/Si pseudosubstrates using metal organic chemical vapor deposition (MOCVD). These Ge/Si pseudosubstrates (PS) were grown by CVD on Si (001) wafers and subsequently chemically-mechanically polished. In order to reduce the number of antiphase boundaries, the GaAs growth was started with atomic layer epitaxy (about 5.6 nm) followed by a low temperature GaAs growth step. Such structures were successfully used as pseudosubstrates for fabricating heterojunction lasers with an active region of GaInAs for near infrared emission. Whereas with atomic force microscopy the surface morphology can be investigated, information on the buried interfaces is difficult to obtain since the usual x-ray reflectivity measurements fail for the Ge/GaAs interface. The reason for this is the fact that the atomic form factors $f = f_0(Q) + f'(E) + if''(E)$ of Ga, Ge and As are nearly identical for conventional 8 KeV x-ray photon energies, since these three elements are neighbors in the same row of the periodic table. However, by measuring close to the Ga K-absorption edge, the form factors for Ga, Ge and As differ substantially so that sufficient material contrast can be achieved. X-ray reflectivity measurements (both specular-scans and reciprocal space maps) were carried out at four different photon energies, namely 10 469, 10 418, 10368, and 10318 eV at the ESRF synchrotron source (Grenoble) at beamline ID01. For these energies the real part of the atomic form factor f' changes from -5.0 (slightly below the Ga K edge) to -2.67. Energies below the Ga K edge were chosen in order to avoid fluorescence radiation. Based on the data analysis of the specularly reflected signal as a function of the momentum transfer along [001] growth direction and the diffuse scattering for finite in-plane momentum transfer, we determined the roughness of the buried Ge/GaAs interface, and its vertical and lateral correlation properties. In particular, it turned out that the r.m.s buried Ge/GaAs interface roughness is of the order of 0.5 nm, whereas the GaAs surface r.m.s roughness varies between 10 and 1 nm for the samples investigated.

Q5.2

Abstract Withdrawn

Q5.3

Grain Misorientation-Location Measurement by Combined use of X-ray Topography with Diffractometry. J.M. Yi¹, Jung

Ho Je¹, Yong S. Chu², H. You³ and W. G. Cullen^{3,4}; ¹Materials Science and Engineering, POSTECH, Pohang, South Korea; ²Experimental Facilities Division, Argonne National Laboratory,

Argonne, Illinois; ³Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ⁴Materials Research Science and Engineering Center, U. Maryland, College Park, Maryland.

Nondestructive probe with sensitivity to both misorientation and location of individual grain has been strongly required due to the importance of local microstructure in studying structural dynamics of a material or its physical properties. We developed a new x-ray diffraction microscopy technique capable of coupling grain misorientation with its spatial location in textured materials. The grain misorientation-location measurement is based on angular-resolved orientation contrast by combined use of x-ray topography with x-ray diffractometry using monochromatic, collimated x-rays. By applying it to Y2O3/Ni, we demonstrated the capability of grain misorientation-location measurement for the textured materials. Its useful applicability for local microstructural analysis was also demonstrated with the observation of the grain-on-grain microstructural correlation between the Y2O3 film grains and the Ni substrate grains. As a result, we found that on surface orientated Ni grains, Y2O3 film grains preferred growing along the crystallographic direction of the Ni(002) grains. On the contrary, on large misoriented Ni grains, Y2O3 grains grew along the surface direction rather than the crystallographic direction of the Ni(002) grains. This result indicates the possibility of different growth mechanisms of Y2O3 film grain, depending on misorientation of substrate Ni grain. This technique is expected to contribute further to understanding of mesoscale phenomena such as phase transformation and plastic deformation of textured materials.

Q5.4

SANS techniques to study cavitation in Zr based superplastic

materials. Steven Van Petegem¹, A. Chokshi³, S. Ghosh³, J. Stahn² and H. Van Swygenhoven¹; 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 exploited 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 materials cavitate during deformation, and excessive cavitation is frequently a leading cause for premature failure in superplastic materials. Cavitation failure is particularly important in superplastic ceramics, and there have been several studies on 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.

Q5.5

Texture Evolution in Triblock Copolymer Network Structures in response to Shear and Uniaxial Deformation as revealed by Small Angle X-ray Scattering. Ralf Kleppinger, DSM Research,

Geleen, Netherlands.

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 1000nm. The network structures, formed by triblock copolymers 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 Kleppinger¹, Michel Koch² and Kell

Mortensen³; 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 structure. 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 provide information regarding the global arrangement of such complexes.

Q5.7 TRANSFERRED TO Q6.2

Q5.8

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

Simultaneous real-time wide and small angle X-ray scattering (WAXS, SAXS) studies 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. Atomic force microscopy of bulk films reveals a 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 on-going to compare structural information on the SGCs with that obtained on the bulk film.

Q5.9

Small-Angle X-Ray Scattering Measurements of Helium Bubbles in Borosilicate Glass. Brent J. Heuser¹, Alexander Y. Terekhov² and Robert S. Averback²; ¹Nuclear, Plasma, and Radiological Engineering, University of Illinois, Urbana, Illinois; ²Materials Science and Engineering, University of Illinois, Urbana, Illinois.

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 BESSRC 12-ID 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 (0.02 < 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. The interference peak was fit with the Percus-Yevick hard sphere model for the structure factor, yielding a bubble radius and bubble volume fraction that both increased with local He concentration. 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 Q3.7

Q5.11

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

The crystalline lamellar structure of isotactic polystyrene (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 phase thicknesses were determined using the one-dimensional electron density correlation and/or interface distribution functions. Time dependent changes in these parameters were correlated to changes in the glass transition temperature, T_g, during crystallization. After spherulite impingement, T_g increases dramatically. More importantly the cooperative length, ζ_A, which indicates the spatial limitation on the large mode length of the glass transition, gets smaller during crystallization. Cold-crystallization of iPS results in reduction of molecular mobility: the formerly liquid-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 T_g. Finally, SAXS results shows that the mobile amorphous layer thickness is larger than cooperative length ζ_A, while the rigid amorphous layer thickness is smaller than ζ_A.

Q5.12

Neutron Reflectivity Study of Lipid Membranes Assembled on Ordered Nanocomposite and Nanoporous Silica Thin-Films. Dhaval A. Doshi¹, Andrew M. Dattelbaum¹, Erik B. Watkins¹, Jaroslaw Majewski¹, Andrew P. Shreve¹ and Atul N. Parikh²; 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 formed on ordered silica thin-films using 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 used here 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-Glycero-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-il Jang¹, Baekyun Kim², Sangkyun Lee² 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 in MLCC, high dielectric constant BaTiO₃ (BT) powders with fine grains are required. MLCCs have to be cofired in a reducing atmosphere to prevent from oxidation of Ni electrode, which results in poor insulation resistance of BaTiO₃ ceramics. Therefore additive doping of BaTiO₃ is of great important for chip products with high reliability in severe environments. At present, Ca becomes one of 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 Ba_{1-x}Ca_xTiO₃ 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. Vincent Leon^{1,2}, Yang Ren¹ and Marie-Louise Saboungi²; ¹IPNS, Argonne National Laboratory, Argonne, Illinois; ²CRMD, CNRS, Orleans, France.

Silver chalcogenides such as Ag_2Se and Ag_2Te are known to be non-magnetic semiconductors at temperatures below 400K, without displaying significant magnetoresistance. However, altering the stoichiometry to accommodate a small amount of surplus silver, the electrical resistance of $\text{Ag}_{2+\delta}\text{Se}$ and $\text{Ag}_{2+\delta}\text{Te}$ (with $\delta = 0.01$) become very sensitive to magnetic field up to 60 Teslas. 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-field sensors. Our work is to confine this kind of material 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 particles 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 ordered array of pores, with a diameter of about 2 nm. In the case of Ag_2Se , 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 standard powder diffraction data set of the orthorhombic structure of Ag_2Se .

Q5.15

Energy Controlled X-ray Filter for Energy Dispersive X-ray Reflectometry. Toshihisa Horiuchi, Keitaro Kago and Kazumi Matsugise; 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. In the specular XR measurement, there are two types of techniques; one is angle dispersive X-ray reflectometry (ADXR) 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 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 ADXR 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 over its detectable ability. Therefore, the reflected X-ray in the higher energy is hardly detected precisely. To solve this problem, we invented the refraction-transmission type X-ray filter. This filter consists of the substrate of low attenuation coefficient and the thin film of high electron density on the substrate. This filter removes the X-rays in the lower energy of the white X-ray selectively by the total reflection and guides the X-ray in the higher energy; the reflection intensity in the lower energy becomes comparable to that in the higher energy range. As the result, the EDXR data are obtained for the wider scattering vector. Even a substrate without a thin film plays the role of the filter. We produced a Be filter experimentally and introduced the filter to EDXR for a silicon wafer. By using this X-ray filter, we obtained the EDXR data for the wider scattering vector.

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, diagnostic techniques capable of producing accurate, sensitive, chemical analysis on the spatial scale of the nanomaterial itself are required. There are currently many materials analysis techniques available to look at surfaces and interfaces. 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 Technologies, Research Division, proposes to use 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 $1.22 \times$ 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 ablate the sample and heat the material to form a nanoplasma. 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 radiation from 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 as opposed to UV from a laser and therefore 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 the instrument can be also 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 nanoscale devices by rastering the material under the nanoplasma. Finally in analogy to plasma assisted CVD processes, organometallic vapors could be introduced into the sample chamber such that the nanoplasma locally plates out specific species of metals or other materials on the target at nanoscale sizes for forming devices, circuits, wires, etc. 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 $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Studied by Pulsed Neutron Diffraction. Shin-ichi Shamoto¹, Toshiyuki Matsunaga², Norobu Yamada², Thomas Proffen³, James W. Richardson⁴, Jae-Ho Chung⁵ and Takeshi Egami⁶; ¹Neutron Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan; ²Panasonic Ltd., Moriguchi, Osaka, Japan; ³LANSCE, Los Alamos National Laboratory, Los Alamos, New Mexico; ⁴IPNS, Argonne National Laboratory, Argonne, Illinois; ⁵Center for Neutron Research, National Institute of Standard and Technology, Gaithersburg, Maryland; ⁶University of Tennessee, Knoxville, Tennessee.

The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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 commercial 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 Fm-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 ($R_{wp} = 10.8\%$ and $R_e = 4.0\%$). We set a periodic non-symmetric cubic unit cell with 8 sites, where one tellurium atom was fixed at the origin. All tellurium occupation factors were fixed to be unity, while the summation of occupation factors of germanium and antimony atoms at all the similar positions of 4(b) site was fixed to be an average value of 0.8. Isotropic thermal factors were assumed to depend only on the elements. Otherwise, all atoms were freely displaced. As a result, Ge-Te bond lengths had much wider distribution than Sb-Te bond lengths. The wide and split Ge-Te bond lengths would be due to the narrower radius of germanium 4p orbital than antimony 5p orbital. As a whole, large displacement of germanium atoms is characteristic in the crystal structure. In conclusion, we have found large displacement of germanium atoms in a crystalline cubic phase of $c\text{-Ge}_2\text{Sb}_2\text{Te}_5$, a commercial high-speed phase-change memory material, by using the PDF method, although the average structure determined by Rietveld analysis was well described by the NaCl-type structure. Usually, such a large lattice distortion has disadvantage for the electronic conductivity. The electronic structure, however, implies that this distortion in addition to the lattice defect reduces only the thermal conductivity, resulting in the effective conversion of light energy to lattice heat in a limited area.

8:45 AM Q6.2

Small angle neutron scattering (SANS) and x-ray reflectivity (XR) as complementary methods to characterize porous films containing micro- and meso-pores. Bryan D. Vogt¹, Rajaram A. Pai², Hae-Jeong Lee¹, Christopher L. Soles¹, Wen-li Wu¹, Eric K. Lin¹ and James J. Watkins²; ¹Polymers Division, NIST, Gaithersburg, Maryland; ²Department of Chemical Engineering,

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 (XR) and small angle neutron scattering (SANS) in conjunction with toluene as a probe molecule. The film pore structure can be probed with SANS. The profile shows a strong Bragg peak corresponding to the correlations between the mesopores templated by the hydrophobic phase. The scattering also shows Debye-type 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 using mixtures of d-toluene and h-toluene vapor. Use of the null contrast solution allows for probing the distribution of pores through partial pressure variation and corresponding capillary condensation. The fraction of micropores in the film can be determined from pressure variation measurements. XR 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 N_2 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 the combination of 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.
Tsuyoshi Kimura¹, Gavin Lawes¹, Takeshi Goto², Yoshinori Tokura², Arthur P. Ramirez³, Ryoichi Kajimoto⁴ and Taka-hisa Arima⁵; ¹Los Alamos National Laboratory, Los Alamos, New Mexico; ²Applied Physics, University of Tokyo, Tokyo, Japan; ³Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; ⁴Neutron Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan; ⁵Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan.

The relationships among magnetism, lattice modulation, and dielectric properties have been investigated for perovskite rare-earth manganites, $RMnO_3$ ($R=Eu, Gd, Tb, \text{ and } Dy$). At room temperature, the $RMnO_3$ have the $Pbnm$ orthorhombic structure which is centrosymmetric. These compounds show a transition to an incommensurate lattice structure at the Néel temperature ($T_N = 53-39K$) for sinusoidal antiferromagnetic ordering, and subsequently undergo an incommensurate-commensurate phase transition. Dielectric anomalies were observed at the respective transition temperatures. For $TbMnO_3$ and $DyMnO_3$, it was 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 K_2SeO_4 . The lattice modulation in the rare-earth manganites can be regarded as a second harmonic of the sinusoidal antiferromagnetic structure. Therefore, it is likely that the ferroelectricity 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 gigantic magnetoelectric and magnetocapacitance effects observed in $RMnO_3$.

9:30 AM Q6.4

Reciprocal-lattice Space Imaging of X-ray Intensities Diffracted from Nanowires. Osami Sakata¹, Akiko Kitano¹, Christopher J. Walker¹, Wataru Yashiro², Kazushi Miki², Shusaku Akiba³, Akifumi Matsuda³, Wakana Hara³ and Mamoru Yoshimoto³; ¹Materials Science Division, Japan Synchrotron Radiation Research Institute (JASRI) / SPring-8, Sayo, Hyogo, Japan; ²Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; ³Materials and Structures laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

Structural investigation is essential for development of nanotechnological materials such as nanoelectronics and nanophotonics. A nanowire structure is particularly interesting since the wire will be one of minimum parts of microelectrical devices. X-ray diffraction is a promising non-destructive method for determining atomic-scale structures. The conventional x-ray diffraction approach through maps x-ray intensities diffracted /

scattered around Bragg conditions in a reciprocal-lattice space. In order to establish a rapid structural characterization method, we have developed an "obvious-at-a-glance analysis" technique for crystalline nanowires.[1] By taking advantage of high-energy and brilliant x rays of SPring-8, rapid measurements were achieved by recording many diffracted intensities under Bragg conditions in the reciprocal-lattice space simultaneously. The measurements were carried out using an x-ray 2-D detector at beamline BL13XU for surface and interface structure determination. The present method maps many sets of limited intensities diffracted around Bragg points and coaxes forth specific structural information such as crystallographic domain sizes and correlation lengths of wires. We will also present sheet-shaped diffraction emanating from ultrathin NiO wires and Si-sandwiched Bi nanolines. [1] O. Sakata et al. Appl. Phys. Lett. 84, 4239 (2004).

9:45 AM Q6.5

Small Angle X-Ray Scattering Reveals CdSe/ZnS Quantum Dot Ordering. Jens Falta¹, Thomas Schmidt¹, Torben Clausen¹, Jan Ingo Flege¹, Sigrid Bernstorff², Gabriela Alexe¹ and Detlef Hommel¹; ¹Institute of Solid State Physics, University of Bremen, Bremen, Germany; ²Sincrotrone Trieste, Basovizza, Italy.

CdSe embedded in ZnSe is the most promising material system for the realization of light emitting devices in the yellow-green spectral region. Especially with respect to the implementation of laser diodes, arrays of CdSe quantum dots have attracted much interest. In this respect, much effort is made to obtain ordered and mono-disperse quantum dot arrays. We present grazing incident small angle x-ray scattering results which show that—apart from a vertical correlation previously found [1]—also a lateral ordering of CdSe quantum dots can be achieved. Vertically stacked CdSe quantum dot layers embedded in strain compensating ZnS spacer layers have been investigated in dependence of different growth parameters. Satellite spots at non-vanishing parallel components of the scattering vector unambiguously reveal a lateral correlation of the quantum dots. From the dependence on the spacer layer thickness and the number of quantum dot layers, it is concluded that the quantum dot ordering is a strain-driven, self organized process [2], as already proposed for other material systems[3-5]. A kinetic limitation of this process is indicated from growth temperature-dependent measurements. Nevertheless these findings imply that the lateral correlation of CdSe quantum dots can be drastically improved by the adequate choice of growth parameters. In addition a two-fold anisotropy of the satellite spots is observed in the scattering data, the origin of which will be discussed. REFERENCES: [1] D. Litvinov, A. Rosenauer, D. Gerthsen, H. Preis, K. Fuchs, S. Bauer, J. Appl. Phys. 89, 3695 (2001) [2] Th. Schmidt, T. Clausen, J. Falta, G. Alexe, T. Passow, D. Hommel, S. Bernstorff, Appl. Phys. Lett. 84, 4367 (2004) [3] J. Tersoff, C. Teichert, M. G. Lagally, Phys. Rev. Lett. 76, 1675 (1996) [4] M. Pinczolits, G. Springholz, G. Bauer, Appl. Phys. Lett. 73, 250 (1998) [5] Q. Xie, A. Madhukar, P. Chen, N. P. Kobayashi, Phys. Rev. Lett. 75, 2542 (1995)

10:30 AM *Q6.6

Novel States in Strongly Correlated Spinel $CuIr_2S_4$.
Valery Kiryukhin, Dept. Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

Spinel $CuIr_2S_4$ is an extremely rare example of 5d-row non-oxide compound exhibiting strong correlations. Its low-temperature state is a charge-ordered spin-dimerized insulator, in which the Ir^{4+} ions form a sublattice of 4-dimer aggregates (the Ir octamers). 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 disordered dimer-liquid state, in which the dimers are confined in certain plains 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 $CuIr_2S_4$. X-rays, therefore, produce an entirely new state in this material. The incommensurate correlations reflect the electronic and lattice effects that are suppressed in the long-range ordered virgin state. A different type of an x-ray-induced transition occurs in Zn-doped $CuIr_2S_4$. 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

Fluctuation X-Ray Microscopy for Study of Medium-Range

Order. Lixin Fan¹, I. McNulty¹, D. Paterson¹, M. M. J. Treacy² and J.M. Gibson¹; ¹Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; ²Department of Physics and Astronomy, Arizona State University, Tempe, Arizona.

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 variations 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 wide range of disordered materials from soft matter to nanowire arrays, semiconductor quantum dot arrays and magnetic materials. It will also help us to understand the mechanisms of order-disorder transition and may lead to control of ordering, which is important in developing ordered structures 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.

11:15 AM Q6.8

In-situ Synchrotron Studies of the Multiscale Phase Transformation Behaviors in Bulk Metallic Glass.

Xun-Li Wang^{1,2}, Fei Zhou¹, Alexandru D. Stoica¹, Ling Yang^{3,1}, C. T. Liu², J. D. Almer¹ 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 multiscale 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 measurements of 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. We have applied this technique to investigate the phase transformation in bulk metallic glass. Our data on $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ showed, for the first time, that the phase transformation in bulk metallic glass proceeds in stages, with distinctively different kinetics. Nanometer sized clusters form first, as revealed by the growth of the small angle scattering intensity. This was followed by an abrupt amorphous-to-crystalline phase transformation within the clusters, as revealed by the sudden appearance of the diffraction peaks. New experiments, at different constant heating rates, confirmed the above observations. Moreover, the new data revealed subtle changes in the diffraction patterns even in the phase separation stage. We interpret these changes as evidence of short-range ordering within the developing clusters. The small angle scattering profile, although starting to rise well before crystallization, exhibits an interference peak only after the diffraction peaks appeared. Below and above the crystallization temperature, the small angle scattering intensity follows different scaling laws with temperature. These scattering data will be discussed in conjunction with the results of DSC measurements. This research was sponsored by Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC05-00OR22725 with UT-Battelle, LLC. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. References [1] X.-L. Wang et al., Phys. Rev. Lett. 91, 265501 (2003)

11:30 AM Q6.9

Structural Characterization of Oriented Single-Walled Carbon Nanotube Materials Using X-ray Scattering*, W. Zhou and J. E. Fischer; MSE Dept., U. Penn., Philadelphia, Pennsylvania.

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 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 (2-D) triangular rope lattice. This is 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 can be easily and accurately quantified. We find that the degree of nanotube alignment varies significantly with synthesis methods and parameters. The best-aligned fibers spun from super-acid suspensions exhibit mosaic spread as narrow as 31° . 26 Tesla-aligned films exhibit an out-of-plane mosaic of 27° and in-plane mosaic of 34° , which are the best values reported for nanotube films. X-ray scattering is also used to study C_{60} filled single-walled carbon nanotube (fullerene peapod) film, which has no in-plane preferred orientation. Here, the finite out-of-plane mosaic enables quantitative separation of one-dimensional diffraction (chains of C_{60} peas) 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.)

11:45 AM Q6.10

Characterization of 2-dimensional CoPt₃ Overlayers With Grazing Incidence Small Angle X-Ray Scattering and Electron Microscopy.

Jan Ingo Flege¹, Thomas Schmidt¹, Roland Kroeger¹, Igor Randjelovic², Vesna Aleksandrovic², Gabriela Alexe¹, Torben Clausen¹, Sigrid Bernstorff³, Horst Weller² and Jens Falta¹; ¹Inst. of Solid State Physics, University of Bremen, Bremen, Germany; ²Inst. of Physical Chemistry, University of Hamburg, Hamburg, Germany; ³ELETTRA Synchrotron Light Source, Trieste, Italy.

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 dots with well-defined electronic properties is very promising. Here 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(acac)₂ and thermal decomposition of Co₂(CO)₈ 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 angle x-ray scattering (GISAXS) experiments were performed at the SAXS beamline 5.2L at the third-generation synchrotron light source ELETTRA (Italy) using 8 keV photons. A CCD 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 inter-particle 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 scanning electron microscopy (SEM) images were obtained to map the local superlattice structure as well as the mesoscopic film morphology. Additionally, transmission electron microscopy (TEM) data will be presented revealing the inner atomic structure of the nanoparticles.

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

Chair: Surita Bhatia

Wednesday Afternoon, December 1, 2004
Hampton (Sheraton)

1:30 PM Q7.1

2D and 3D X-Ray Structural Microscopy Using Submicron-Resolution Laue Microdiffraction. John D. Budai¹, Wenge Yang¹, B. C. Larson¹, J. Z. Tischler¹, Wenjun Liu² and G. E. Ice¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²UNICAT-UIUC, Argonne, Illinois.

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

developed a scanning, polychromatic x-ray scattering technique with submicron spatial resolution on the UNICAT beamline (sector 34) at the Advanced Photon Source. In this technique, white 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 the local lattice structure, crystallographic orientation, and the strain tensor. These microdiffraction capabilities have enabled both 2D and 3D structural studies of materials on mesoscopic length-scales of tenths-to-hundreds of microns. For thin samples such as deposited films, 2D 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 aluminum 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}, E. T.

Lilleodden^{1,2}, N. Tamura³, J. Florando⁴, D. Lassila⁴, R. Barabash⁵ and J. W. Morris^{1,2}, ¹Department 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; ⁴Engineering Directorate, Lawrence Livermore National Laboratory, Livermore, California; ⁵Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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 understand the deviation from the expected single slip result 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 presented, and compared to experimental data. Preliminary results include orientation maps from a highly strained Ta 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 structure 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. Saleh^{1,2}, Bjorn Clausen², Hahn Choo^{4,3}, Don W. Brown², Raymond A. Buchanan¹, Peter K. Liaw¹ and Dwaine L. Klarstrom⁴; ¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²Los Alamos Neutron Science Center, Los Alamos National Laboratory, Los Alamos, New Mexico; ³Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ⁴Haynes International, Inc., Kokomo, Indiana.

Haynes 230 is a solid solution strengthened, face centered cubic (FCC), nickel based superalloy, with a small percentage of semi-coherent FCC carbides. This alloy has a tension-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 (1-5%), the carbides had a significant effect on the load sharing during loading. In both 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 Integrative Graduate Education and Research Training (IGERT) Program, under DGE-9987548, and the International Materials Institutes (IMI) Program under DMR-0231320, and the Combined Research-Curriculum Development (CRCD) Program, under EEC-9527527 and EEC-0203415, with Drs. P. W. Jennings, L. S. Goldberg, L. Clesceri, C. Huber and Ms. M. Poats as contract monitors.

2:15 PM Q7.4

In-Situ Neutron Diffraction Study of Strain-Induced Martensite Formation and Its Deformation Behavior at a Cryogenic Temperature. Kaixiang Tao¹, James J. Wall¹, Donald

W. Brown², Sven C. Vogel², Mark A. M. Bourke² and Hahn Choo^{1,3}; ¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²MST-8, Los Alamos National Laboratory, Los Alamos, New Mexico; ³Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

In-situ, time-of-flight neutron diffraction was performed to investigate the strain-induced martensitic phase transformation during quasi-static uniaxial compression testing of 304L stainless steel at 300K, 268K, and 203K. The in-situ neutron diffraction study provides bulk measurements of the evolution of phase fractions, texture, and lattice strains during the austenite (fcc) to martensite (bcc) phase transformation. The extent of the transformation is dependent on the testing temperature and amount of applied strain. The Rietveld analyses show that the martensite volume fraction increases almost linearly starting at about 2.5% applied strain (i.e., 600MPa applied stress) at 203K. However, at 300K, the martensite formation was not observed throughout the test. The hkl-specific lattice strain evolution in directions parallel and perpendicular to the loading axis shows typical polycrystalline elastic/plastic anisotropy in all cases. Furthermore, the load partitioning between the austenitic matrix phase and the newly-forming martensite phase at 203K shows significant load re-distribution from the austenite to martensite phase above 600MPa. The results provide micromechanical understanding of the strain-hardening behavior of the alloy undergoing strain-induced martensitic phase transformation.

2:30 PM Q7.5

Probing Mesoscopic Strain Evolution during Creep Deformation: An In-Situ Neutron Diffraction Study.

Hahn Choo^{1,2}, Donald W. Brown³ and Mark A. M. Bourke³;

¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Materials Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico.

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, at the SMARTS beamline at the Los Alamos Neutron Science Center. The hkl-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 accumulation 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 rotation and the relatively slower strain rate during the creep compared to the quasi-static testing.

2:45 PM Q7.6

The Use of Time-of-Flight Neutron Diffraction to Study Stress Induced Transformation and Reorientation in Shape Memory Alloys. Donald William Brown¹, Mark A. M. Bourke¹,

Sven C. Vogel¹, David F. Teter¹, Daniel J. Thoma¹, L. Cate Brinson², Xiugie Gao², Raj Vaidyanathan³ and Chandra Rathod³;
¹Materials Science and Technology, Los Alamos National Lab, Los Alamos, New Mexico; ²Northwestern University, Evanston, Ohio; ³University of Central Florida, Orlando, Florida.

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 bulk penetration and the continuous incident spectrum utilized at spallation 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, nickel-titanium and uranium-niobium, using the SMARTS and HIPPO diffractometers at the Los Alamos Neutron Science Center. The technique affords information about the transformed and/or twinned volume fraction as a function of deformation as well as load sharing between the phases/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. Emil Zolotoyabko¹, Boaz Pokroy¹ and John Quintana²; ¹Materials Engineering, Technion, Haifa, Israel; ²DND-CAT Synchrotron Research Center, Northwestern University, Argonne, Illinois.

Characterization of the microstructure of materials with high spatial resolution is one of the key issues 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 much larger. As partial solution, 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 accurately control 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 lamella size and microstrain 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 treated 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 artificial multilayered structures and inhomogeneous structures from nature (seashells) demonstrate the capabilities of the method. [1] E. Zolotoyabko and J. P. Quintana. Non-destructive microstructural analysis with depth resolution: Application to seashells. *J. Appl. Cryst.*, v. 35, 594-599 (2002). [2] E. Zolotoyabko and J. P. Quintana. Non-destructive microstructural analysis with depth resolution. *Nucl. Instr. Meth. B*, v. 200, 382-389 (2003). [3] B. Pokroy and E. Zolotoyabko. Microstructure of natural plywood-like ceramics: a study by high-resolution electron microscopy and energy-variable X-ray diffraction. *J. Materials Chemistry*, v. 13, 682-688 (2003).

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 statistically 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 kinds 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 also strongly correlated long range rotations within the crystal, grain, or subgrain. Non homogeneous 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 space vector of each reflection. Diffracted 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 local 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 the two 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 Diffractometry. J.M. Yi¹, Seong Kwon Seol¹, Jin Xiao¹, Jung Ho Je¹, T. S. Argunova² and Yeukuang Hwu³; ¹Materials Science and Engineering, POSTECH, Pohang, South Korea; ²Ioffe Physico Technical Institute, Russian Academy of Sciences, St. Petersburg, Russian Federation; ³Institute of Physics, Academia Sinica, Nankang, Taiwan.

We investigated the misfit dislocation (MD) nucleation and the dislocation morphology in lightly boron-doped Si epitaxial layers (20 Ωcm) on heavily boron-doped Si (001) wafer (0.015 Ωcm) (p/p+ Si) using white beam diffraction microscopy (WBDM) and high resolution x-ray diffractometry (XRD). The strain-relaxing MDs start to nucleate from the wafer edge and proceed to the center. Interestingly a dislocation slip-band morphology together with an orthogonal array of $\langle 110 \rangle$ type dislocations is able to be observed by WBDM, which has not been reported by conventional x-ray topography. The dislocation slip-bands are misoriented each other as measured by XRD. The misorientation 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 topographs. 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 epitaxial layer.

4:15 PM Q7.10

Internal Strain Measurements and X-ray Radiography in Interpenetrating-Phase $\text{Al}_2\text{O}_3/\text{Al}$ Composites. Marcus L. Young^{1,2}, J. D. Almer², U. Lienert², K. Fezzaa², W. K. Lee², D. R. Haefner², R. Rao³, J. A. Lewis³ and D. C. Dunand¹; ¹Materials Science & Engineering, Northwestern University, Evanston, Illinois; ²Argonne National Laboratory Advanced Photon Source, Argonne, Illinois; ³Materials Science & Engineering, University of Illinois, Urbana, Illinois.

Interpenetrating $\text{Al}_2\text{O}_3/\text{Al}$ 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 elastic, 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 $\text{SiO}_2/\text{Si}(001)$ Interface Revealed by the Phase-Sensitive X-ray Diffraction Technique. Wataru Yashiro^{1,2}, Kazushi Miki^{1,2}, Kazushi Sumitani³, Toshio Takahashi³, Yoshitaka Yoda⁴, Kensuke Takahashi⁵ and Takeo Hattori⁵; 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), the University of Tokyo, Kashiwa, Chiba, Japan; ⁴Japan Synchrotron Radiation Research Institute (JASRI), Mikazuki-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 SiO_2/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 SiO₂/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 SiO₂/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. Nakatani, 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 Iqbal¹, N. H.

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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. TiB₂, TiAl₃). 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 TiB₂ particles, separately and together. The role played by TiB₂ 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 TiB₂ 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 TiAl₃ phase that nucleates before the solidification of aluminium starts. It is proposed that in the presence of solute titanium, TiB₂ particles cause the TiAl₃ 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 aluminum grains is found to increase for higher cooling rates. The observed growth curves of the newly formed aluminum 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.