SYMPOSIUM Q
Neutron and X-Ray Scattering as Probes of Multiscale Phenomena
November 29 - December 1, 2004

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Proceedings to be published in both
book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as volume 840
of the Materials Research Society
Symposium Proceedings Series.

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

8:30 AM Q1.1
Application of High Energy X-rays to Quantitative Measurements of Reciprocal Space: Superstructure and Charge Ordering in Nd1BaCo2O5-
Peter Chupas1, Stephan Rosenkranz1, Raymond Osborn3, John F. Mitchell2 and Peter L. Lee2; 1Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 2Experimental Facilities Division, Argonne National Laboratory, Argonne, Illinois; 3Argonne National Laboratory, Argonne, Illinois.

Many new phenomena of considerable technological importance are driven or strongly enhanced by disorder and the nanoscale self-organization that accompanies it. A powerful probe of such defects, 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 removing the need to eliminate the Bragg peaks 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 for 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 reliability 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 Nd1BaCo2O5-

8:45 AM Q1.2

Relaxor ferroelectric oxides, such as Pb(Mg1/3Nb2/3)O3 (PMN), show a diffuse maximum of dielectric susceptibility at the freezing temperature. Susceptibility peak is frequency dependent with a broad relaxation spectrum. The diffuse transverse Raman scattering measured at presence of local polar domains above formal Tc, 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 Tc and disappears at the so called Burn's temperature about 630 K. We have measured dynamic structure factor S(Q,w) for PMN at three temperatures, in the proximity of Burn's 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, however 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 Burn's temperature.

9:00 AM *Q1.3
Revisiting the ground state of an insulating, half-doped manganite with resonant x-ray scattering, Jessica Thomas1, John Hill1, Stephane Grenier1, Peter Abbamonte1 and Michel van Veenendaal2, 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 ordering of Mn sites in a number of half-doped, insulating manganites. In this picture, proposed by Goodenough to explain the complex "CE" type magnetic ground state, distinct sub-lattices of Mn3+ and Mn4+ sites form at Tc. The Mn3+ sites are John-Teller active and a cooperative lattice distortion and orbital ordering of the Mn3+ sites occurs at the same temperature as the charge ordering. Magnetic ordering occurs either coincident with, or below, the charge-orbital order transition temperature. However, the dynamics which lead to this particular ordering are still not understood. For example, it is unclear whether it is the magnetic interactions which stabilize the orbital and charge order or the charge and orbital order is simply a precursor to the magnetic ground state. Furthermore, the degree to which the charge separation into Mn3+ and Mn4+ sites is complete remains a controversial issue. Resonant x-ray scattering near the atomic Mn LIII absorption edges (2p -> 3d) is a powerful probe for studying orbital and spin correlations in manganites. At the Mn L-edges (~590 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 allow a direct comparison of orbital and spin correlations in the near-half-doped manganite Pr0.6Ca0.4MnO3. Comparing the widths of the magnetic, Q = (1/2,0,0), and orbital, Q = (0,1/2,0), diffraction peaks we find 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 lines. This 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 which suggests that Mn3+ 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 Lob0; 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 averaging way. At the atomic level methods such as solid state NMR and optical spectroscopies are used to gain knowledge about the local chemical environments and geometry surrounding selected atoms in a sample. However, these approaches do not help solve problems associated with understanding diffusion and the catalytic and adsorptive properties of zeolites, mainly because the need of precise atomic models to understand these questions. 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 polypeymas A and B. Both of this polypeymas have an identical layer of pores that is stacked differently in the c direction. This layer is extended infinitely in a ab and has a height of approximately 7 A along the c direction. Thus, the structure of polypeymas were refined using neutron and synchrotron data up to 7 A. Refinements using only the synchrotron or the neutron datasets gave results inconsistent with each other but a cyclic refinement of the two datasets gave a good fit to both PDFs. The result shows that the PDF method is valid 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. By using synchrotron PDF at room temperature and at 78K. Preliminary results show that the structures of the tetrahedra are unchanged with temperature suggesting that the mechanism is likely to be some motion between tetrahedra.
Typical metallic glasses are obtained by rapid quenching from a melt with cooling rates on the order of 10^5-10^6 K/s. Below the glass transition temperature, viscosity increases by several orders of magnitude and the supercooled liquid forms a glass. The resultant glass is metastable: it can transform to the 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, electronic, and magnetic properties and can be studied by neutron and x-ray scattering. Bulk-metallic glasses (BMGs) are special compositions of metallic glasses that can form massive (bulk) glasses alloys with very low cooling rates (~1 K/s). Since the cooling rate is so low, one would expect the low temperature annealing would have a very small effect on the structure. Surprisingly, we can observe pronounced changes in the local atomic structure as described by the pair distribution function (PDF). A BMG alloy with a nominal composition of Zr52.5Cu17.5Ni14.6Al8.0 (at. %), commonly known as Vitreloy 105 (Vit 105), was prepared by arc-melting and drop-casting in a water-cooled mold under Ar atmosphere. Neutron diffraction studies were conducted on the General Purpose Powder Diffractometer (GPPD) 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 relaxation was 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 at the Intense Pulsed Neutron Source (IPNS), and x-ray studies were conducted in 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. Acknowledgments.

This work was supported by the National Science Foundation (Grant No. DMR-0231320, Dr. C. Huber).

Structure and dynamics of water adsorbed in carbon nanotubes: A joint neutron-scattering and molecular-dynamics study, Nicola R. de Souza 1, Alexander I. Kolesnikov 2, Chun K. Loong 1, Alexander P. Morovsky 3, Rouf O. Looty 4, and Christian J. Burnham 1, 1, Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois; 2, Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada; 3, Henry Eyring Center for Theoretical Chemistry, University of Utah, Salt Lake City, Utah. The advent of nanocarbons, from single- and multi-walled nanotubes to nanohorns, allows 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 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 opened-end single- and double-walled nanotubes over a wide range of spatial and temporal scales. We find that a square-ice sheet wrapped next to the inner nanotube wall and a water chain in the interior are the key structural elements of nanotubes-confined water/ice. This configuration results in a hydrogen-bond connectivity that markedly differs from that in bulk water. This significantly slows down the hydrogen-bond network manifests in neutron-diffraction studies and indicates a new 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.

The coupling of spin and orbital degrees of freedom in a layered rutheniate: An inelastic neutron scattering study, Ray Osborn 1, Peter Khalifah 2, Stephen E. Nagler 3, and Mark D. Langfelder 4, 1, Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 2, Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

There is considerable evidence of the influence of orbital degrees of freedom on the magnetic properties of ruthenate compounds. The layered ruthenate compound, La4RuO6, provides a particularly good example. The structure comprises corner-shared RuO6 octahedra forming corrugated layers. At 10K, 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 3d4 4f electrons. The magnetic susceptibility exhibits a peak at the transition. Inelastic neutron scattering on both polycrystalline and single-crystal samples has shown that this is associated with the formation of a singlet ground state. Above the transition, the scattering is broad and quasielastic, consistent with the presence of spin fluctuations within the S=1 ground state. Below the transition, a spin
findings from quasielastic neutron scattering (QENS) of specific configuration of O and H may be important in the energy for guest rotation that is higher in the high-temperature clathrate hydrate (CH) comprises water molecules held together by compounds that occur in nature in vast deposits under the ocean floor occur in the host as a function of temperature. (2)

change in orbital configuration induces local singlets, which are changes in the guest dynamics is proposed. 1. Makagon, coupled by interionic exchange, or the singlets are themselves formed 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·1.72H2O. The QENS results show a reduction in the 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. Malagon, Y. E., Trebin, P. A., Trolmalm, A. A., Tsarev, V. P., Charsky, N. V., Doli, Acad. Sci. USSR – Earth Sci. Sect. 1972, 196, 197-200. 2. Jones, C. Y.; Marshall, S. L.; Chakoumakos, B. C.; Rasen, C. J.; Ishii, Y. “Structure and Thermodynamic 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. Livingston1; 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 50-70 wt.% 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 performed, 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 to the pore space, in a way the cement paste. Here we report the interaction of hydrating tricalcium and dicalcium silicates by QENS. Mixtures of synthetic tricalcium and dicalcium silicates 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 D. Keung Long1, Christopher L. Soles and Marcus T. Cicerone; Polymers Division, NIST, Gaithersburg, Maryland; 2University of Maryland, College Park, Maryland.

Although the existence of various carbon nano-materials has been known for some time, the investigation of their vibrational spectra was mainly limited to the use of optical spectroscopy. In spite of the well-recognized advantages of inelastic neutron scattering (INS) technique, namely, unrestricted by the selection rules of infrared and Raman spectroscopy and accessible to all vibrational modes in the reciprocal space, so far this method was used for the study of only fullerenes and single-walled carbon nanotubes (SWNT). Here we present the INS measurements on a series of carbon nano-materials; SWNT (14 A diameter), double-walled carbon nanotubes (DWNT of 25 A 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 glassy state of these compounds mimics water in terms of its thermodynamic interactions, it 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 proteins dynamics at a 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 proton 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. Akos Szolnoky, Department of Polymer Science, The University of Akron, Akron, Ohio.

Hydrated proteins and DNA demonstrate a dynamic transition at temperatures Td 200-260K. It shows up as a sharp rise of mean-square 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

3:30 PM Q2.6
A Small Angle Neutron Scattering Study of Protein Filaments F-actin. Jay X Tang1, Jorge Viamontes2, Qi Wen3 and Jyotsna Lall4, 1Physics, Brown University, Providence, Rhode Island; 2Argonne National Laboratory, Chicago, Illinois.

The cytoskeletal protein actin self-assembles to form long and stiff filaments, F-actin, which serves essential functions in cells, such as control of cell shape, division, and motility. We have performed a small angle neutron scattering study with an aim to determine the hydrodynamic cross-sectional radius of F-actin in various ionic conditions. Reliable values were obtained using the contrast matching technique by measuring the scattering profile with various D2O/H2O mixtures. Since F-actin undergoes the isotropic-nematic (I-N) liquid crystal transition at a temperature lower than 15°C, the scattering patterns of large ordered domains of F-actin were also obtained. Due to the large scattering area on the order of a square centimeter but on the other hand limited sample volume available, there has not been an effective 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. Q. Guo1,2, M. Correa1, C. Converse1, Paul D.辨ier3 and Lionel Porcar4, 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 nanoscale 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 networks 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

Alumina/poly(methylmethacrylate) (PMMA) nanocomposites synthesized by in situ free-radical polymerization in the presence of 38 nm alumina nanoparticles exhibit a novel percolation-like transition at about 1 vol% filler concentration [1]. This phenomenon is accompanied by a brittle-ductile transition with a large increase in the ‘strain-to-failure’. In silica/poly(vinylacetate) 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, we have used neutron scattering spectroscopy (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 composite show a large degree of orientation 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 aggregation of about 220 nm, 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 [3]. XPCS measurements after 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). [2] R. A. Narayanan et. al, unpublished. [3] R.A. Narayanan et. al, unpublished.
measurements showed that the copolymers exhibited a distinct scattering maximum when the FOSA composition was above 5 mol%.

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8:30 AM Q3.1

Crystallographic Texture in Pt/Si Structures Measured with Conventional and Synchrotron X-Ray Techniques.

Mark Vaudin1, Jan Hlavsky2 and Glen Fox3

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2XOR, Advanced Photon Source, Argonne National Laboratory, 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 mm (001) Si wafers has been characterized by various diffraction techniques, primarily x-ray. Parallel beam and off-axis 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 2×10 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 defocussing and absorption. The comparisons between these data sets provide vital information in the development of a thin film texture standard. The relative accuracies and precision of the data sets give interesting insights into the relative strengths and the complementary nature of these two approaches to texture measurement. The utility of electron backscatter diffraction in texture measurements in highly oriented materials will be discussed.

8:45 AM *Q3.2

X-ray scattering: a wonderful tool to probe lattice strains in materials with small dimensions. Olivier Thomas

In-situ Deformation Studies at the Swiss Light Source.

11:00 AM Q3.6

In-situ Deformation Studies at the Swiss Light Source.

Helena Van Suygenhoven, 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 localized, 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 diffraction profiles and the evolution of the peak profile with strain direction.
the peak broadening during plastic deformation of electroplated nanocrystalline Ni (Science 304(2004)273) and the applicability to measure elastic and plastic properties from thin films of a few microns and less. Furthermore, it will be shown how X-ray spectra derived from atomistic simulated nanocrystalline samples can help understand measured diffraction spectra.

11:15 AM Q3.7

A planar magnetron sputter deposition system was constructed on top of a XRD diffractometer for real-time observation 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 sensitive to gas pressure or plasma power. 5) Derived from atomistic simulations and nanocrystalline samples can help understand the growth of tantalum films. 3) Substrate species affect phase of tantalum film during nucleation and growth. However, film can change phase during growth with no apparent external interference. 4) In the range of 9-100Watts, 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.

11:30 AM *Q3.8
Anisotropic USAXS from Stretched Filled Polymers, Thomas Rieker1, Pete Jemain2 and Jan Ilavsky2, 1 Div. 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 Bone-Hart instrument at the APS. The utility of the 2-D Bone-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$_2$-Sr$_x$RuO$_4$; relation between crystal structure and physical properties, Markus Branden1, Oliver Breit2, 1, 2, Olaf Schuman2, 1, 2, Björn2, 1, 2, Steffens2, 1, 2, Kiener1, 1, 2, Olaf2, 1, 2, Raddi2, 1, 2, Nakata2, 1, 2, Maeno2, 1, 2, Universitaet zu Koeln, II. Physikalisches Institut, Koeln, Germany; 2Laboratoire Leon Brillouin, Gif-sur-Yvette CEDEX, France; 3IRIS Facility, Chilton, Didcot, United Kingdom; 4Kyoto University, Kyoto, Japan.

Substituting the Sr in the spin-triplet superconductor by Ca yields an extremely 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, Ca$_2$RuO$_4$, is an antiferromagnetic Mott-insulator. Several distinct phenomena are driven by several structural distortions associated with tilting and rotating of the RuO$_6$ 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 "He Analyser, Wai- bullpen Chen1, 2, Kevin O’Donovan1, 2, 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 spinmirrors 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 spin-polarized spin PNR analyzers have limited angular acceptance. Polarized "He 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 "He. "He 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 "He analyzer in conjunction with a position-sensitive detector (PSD). We obtained spin-analyzed two-dimensional Qx-Qz reciprocal space maps for a patterned array of Co antidots in the saturated and the demagnetized states. Data obtained from a "He analyzer and a PSD were compared with those obtained from a conventional spin-polarizer analyzer, and show good agreement between them. The preliminary results for the upcoming experiments with a "He 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 roughtness. Whereas the magnetization depth profile can be obtained from specular PNR, diffuse PNR is needed to obtain information on lateral magnetic domains and magnetic roughtness. The result of our 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 "He spin-polarizer: 1) "He polarization and long polarization storage time of the cell. Using a spectrally narrowed diode laser array we have recently achieved "He polarizations of 74% to 77% in "He cells ranging from 260 cm$^{-2}$ to 500 cm$^{-2}$ volume. At 75% "He polarization, an analyzing efficiency of 0.07 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 Ptilathalocyanine, James E. Downes1, Cormac McGinness2, 1, 2, 3, Ted Andero O1, 1, 2, Timothy Learmonth1, 1, 2, 3, Yifeng Zhang 1, 2, 3, Korinna Smith1, 1, 2, 3, Department of Physics, Boston University, Boston, Massachusetts; 2School of Chemical and Physical Sciences, Victoria University, Wellington, New Zealand; 3Department of Physics, Trinity College Dublin, Dublin 2, Ireland.

We report a synchrotron radiation-exited 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 damaged 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 resonant 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 crystalline systems, since it allows one to probe the underlying electronic structure. Supported in part by the donors of the Petroleum Research Fund, administered by the ACS, and by the NSF under DMR-0309490. Our spectrometer is funded by the U.S. ARO under DARPA-011-01-0564 and DARPA-011-04-0511. Experiments were performed at the NSLS which is supported by the U.S. DOE, Division of Materials and Chemical Sciences. 1. J. E. Downes, C. McGinness, P. A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K. E. Smith, Chem. Phys. Lett. 390, 204 (2004).
The properties of the Na\textsubscript{x}CoO\textsubscript{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 high-temperature superconductivity is induced in Na\textsubscript{x}CoO\textsubscript{2} when it is intercalated with water. We performed inelastic x-ray scattering to characterize the crystal structure and lattice dynamics, and relate these to the observed physical properties. The basic structure of Na\textsubscript{x}CoO\textsubscript{2} is hexagonal and consists of robust layers of CoO\textsubscript{2} interpenetrated 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=\frac{1}{2} where both sites have equal occupancies of \frac{1}{2} 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 electronic configuration, the water forms two additional layers between the Na and CoO\textsubscript{2}, increasing the c-axis lattice parameter of the hexagonal P6\textsubscript{3}\_mmc space group from 11.16 \text{\AA} to 19.5 \text{\AA}. The Na ions are found to occupy a different configuration than expected from the Na\textsubscript{x}CoO\textsubscript{2} parent compound. In contrast, the water forms a structure that replicates the structure of ice to a good approximation. We find a strong inverse correlation between the CoO\textsubscript{2} layer thickness and the superconducting transition temperature (T\textsubscript{c}) increases with decreasing this coherence length, and T\textsubscript{c} is zero for Na\textsubscript{x}CoO\textsubscript{2} when x=\frac{1}{2}. This is also supported by inelastic x-ray scattering measurements. These findings extend over a rather large concentration range 0 < x < 0.15 is three-dimensional. The superconducting transition temperature (T\textsubscript{c}) increases with decreasing this coherence length, and T\textsubscript{c} is zero for Na\textsubscript{x}CoO\textsubscript{2} when x=\frac{1}{2}. This is also supported by inelastic x-ray scattering measurements. These findings extend over a rather large concentration range 0 < x < 0.15 is three-dimensional.
experimentally and theoretically. Understanding the oxidation mechanism is important for practical purpose in many cases, since thin oxide films can serve as protective 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 oxide 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, the oxidation rate 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 Pecharsky
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 Wintersberger, Julian Stangl, Tobias Schueli, Mojmir Meduna, Guenther Bauer, Yves Chirol, Ludovic Largue, Isabelle Sagnes, Guillaume Saint-Girons, Daniel Benedek, Yves Camps, Olivier Kermarrec, Semiconductor physics, Johannes Kepler university, Linz, Austria; 2LPN, CNRS, Marcoussis, France; 3ST Microelectronics, Creles, France.

We studied the structural properties of GaAs layers which were deposited on Ge/Si pseudostructures using metal organic chemical vapor deposition (MOCVD). These Ge/Si pseudosubstrates (PS) were grown by CVD on Si (001) wafers and subsequently chemically-chemically-polished. In order to reduce the number of antiphase boundaries, the GaAs growth was started with atomic layer epitaxy (about 3.0 nm) followed by a low temperature GaAs growth step. Such structures were successfully used as pseudostructures for fabricating heterostructure lasers with an active region of GaInAs for steady-state, we estimate the potential drop at the metal/oxide step. Such structures were successfully used as pseudosubstrates for specularly reflected x-ray scattering experiments. The dynamic range of the x-ray reflectivity measurements is limited to the energies below the Ga K edge and the Ge K absorption edge, the form factors for Ga, Ge and As differ substantially so that sufficient material contrast in x-ray reflectivity measurements (both specular- and reciprocal space maps) were carried out at four different photon energies, namely 10.469, 10.418, 10.368, and 10.318 eV at the ESRF synchrotron source (Grenoble) at beamline ID01. For these energies the real part of the atomic form factors $f$ change from -5.0 (slightly below the Ga K edge) to -2.67. Energies below the M 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 (100) 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


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 in 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 oriented 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 Petegem, A. Chokshi, S. Ghosh, J. Stahn and H. Van Swygenhoven, 1NUM/ASQ, Paul Scherrer Institut, Villigen PSI, Switzerland; 2NUM/LNS, Paul Scherrer Institut, Villigen PSI, Switzerland; 3Department of metallurgy, Institute of Science, Bangalore-40012, 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 metals cavitate during deformation, and excessive cavitation can frequently lead to 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.


Recrystallization 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 macroscopic ordering at length scales between 1 and 1000 nm. The network structures, formed by triblock copolymers in solution represent a rather complex case since in such systems a (re)ordering is caused by the presence of physical crosslinks. Time-resolved small angle X-ray scattering experiments allow insight, not only into the structure of the ordered macromolecular structures but provide moreover the possibility to directly assess the evolution in overall arrangement under the influence of shear or uniaxial deformation.

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

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

**Q5.7 TRANSFERRED TO Q5.2**

**Q5.8**

**Real-Time X-Ray Scattering Studies of P(VDF-TrFE) Copolymers: Comparison of Bulk Film and Solution Grown Crystals.** Bedirion Sebayan 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 kinematics 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. Wide angle X-ray diffraction of bulk films reveals morphology comprising lamellar bundles and larger scale domains. SAXS analysis shows that in SGCs the Bragg spacing is shorter, indicating much thicker lamellae, in both paraelectric and ferroelectric phases, compared to bulk film. Morphology studies are presently ongoing to compare structural information on the SGCs with that obtained on the bulk film.

**Q5.9**


Small-angle x-ray scattering (SAXS) measurements have been performed to investigate He bubble formation in borosilicate glass. The purpose of the experiments is to better understand the performance of glass as a radionuclide waste storage medium. The 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 recoils that occur 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 Q5.7**

**Q5.11**

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

The crystalline lamellar structure of isotactic 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, Tg, during crystallization. After spherical impingement, Tg increases dramatically. More importantly the cooperative length, λ, which indicates the spatial limitation on the large mode length of the glass transition, gets smaller during crystallization. Cold-crystallization of IPS in bulk eliminates the 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 Tg. Finally, SAXS results show that the mobile amorphous layer thickness is much larger than the cooperative length λ, while the rigid amorphous layer thickness is smaller than λ.

**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. Watkins2, Jaroslav Majewski3, Andrew P. Shreve1 and Atul N. Parikh1; 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 via 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.** Youngil Jung1, Baeukyun Kim2, Sangkyun Loe2 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 MLCC, BaTiO3 dielectric constant powders with fine grains are required. MLCCs have to be cofired in a reducing atmosphere to prevent from oxidization of Ni electrode, which results in poor insulation resistance of BaTiO3 ceramics. Therefore additive doping of BaTiO3 is of great 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, tetragonal phase defined by c/a lattice ratio is widely used. However, because of broadening of x-ray peaks, nano BaTiO3 powders with Ca dopant (BCT) are difficult to evaluate the dielectric properties in the stage of producing process. In this research, the influences of solid solution Ba1-xCaxTiO3 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.** Suwon Choi1,2, Yang Ren and Marie-Louise Saboungi1, 1JPNS, Argonne National Laboratory, Argonne, Illinois; 2CRMD, CNRS, Orleans, France.
Silver chalcogenides such as Ag₃Se and Ag₃Te are known to be non-magnetic materials at room temperature without displaying significant magnetoresistance. However, altering the stoichiometry to accommodate a small amount of surplus silver, the magnetic resistance of Ag₃₊δSe and Ag₃₊δTe (with δ = 0.01) becomes very sensitive to magnetic field up to 60 T. 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 metamaterials. Our work is based on 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 ideal recipe for producing particles with dimensions below the critical size of Ag₃Se, 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 Ag₃Se.

Q5.15 Energy Controlled X-ray Filter for Energy Dispersive X-ray Reflectometry. Yoshinori Hosokawa, Keitaro Kago and Kazumi Matsusuga; 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 XR measurements, we use two different 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 reflection-transmission type X-ray filter. This filter consists of the substrate of low attenuation coefficient and the thin film of high attenuation coefficient. This filter removes the X-rays in the lower energy of the white X-ray so 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 a 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 produce 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.

Nanomaterials 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 and to diagnose their chemical composition, 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, but 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, new techniques are required. Taking advantage of 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 1.2λ/2. While 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 make a laser ablation plasma, our work has shown that the x-ray 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 at wavelengths below 1 nm. The emitted plasma 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 rather than 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, XPS and PEEM can be used as well. In addition to diagnostic capabilities it can also be used as a tool to form structures at nanometer scale resolution. Since the plasma is formed by ablating the target material with x-rays the target can be patterned or nanomachined using the plasma itself. It should be possible to pattern nanoscale features using this technique.

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 Ge₅Sb₂Te₅ Studied by Pulsed Neutron Diffraction. Shin-ichi Shamoto1, Toshiyuki Matsusuga2, Noboru Yamada2, Thomas Prouten2, James W. Ralston1, Jae-Koo Chung2, Hiroki Komatsubara1, Hiroshi Shimomura1, 1National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan; 2Panasonic Ltd., Moriguchi, Osaka, Japan.

The Ge₅Sb₂Te₅ 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) analysis. 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 (4a) site is entirely occupied by tellurium atoms, only Ge-Te and Sb-Te bonds appear in the first peak. The obtained G(r) pattern was successfully fitted under the following restriction Rwp = 10.8% and Rfactor = 6%. We set a periodic model of the symmetrically equivalent 16 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 phase of Ge₅Sb₂Te₅, 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 energy light to lattice heat in a limited area.

8:45 AM Q6.2 Small angle neutron scattering (SANS) and x-ray reflectivity (XR) as complimentary methods to characterize porous films containing micro- and meso-pores. Bryan D. Vogt1, Rajaram A. Pai2, Hae-Jeong Lee1, Christopher L. Solens1, 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 to show an extra dimer-liquid state, in which the dimers are confined in 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 have the orthorhombic structure which is centrosymmetric. These compounds show a transition to an incommensurate lattice structure at the N\textsubscript{S} ordering temperature, T\textsubscript{N}\textsubscript{S} = 53 K for sinusoidal antiferromagnetic ordering, and subsequently undergo an incommensurate-commensurate phase transition. Dielectric anomalies were observed at the respective transition temperatures E\textsubscript{h}, D\textsubscript{h}, and D\textsubscript{m} = 2.0 D, 1.7 D, and 1.3 D, respectively. 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 improperferroelectrics such as K\textsubscript{2}SeO\textsubscript{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 giant magnetoelectric and magnetocapacitance effects observed in R\textsubscript{3}MnO\textsubscript{3} (R = Eu, Gd, Tb, and Dy).

9:30 AM *Q6.4


10:30 AM *Q6.6

Novel States in Strongly Correlated Spinel CuIr\textsubscript{2}S\textsubscript{4}, Valery Knyazkin, Dept. Physics and Astronomy, Rutgers University, New Brunswick, New Jersey.

Spinel CuIr\textsubscript{2}S\textsubscript{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\textsuperscript{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-state, in which the dimers are confined in certain planes in the crystal structure. The x-ray-induced state exhibits short-range incommensurate correlations. Interestingly, no incommensurate state is known to exist in the phase diagram of either pure or doped CuIr\textsubscript{2}S\textsubscript{4} X-rays, therefore, produce an entirely new state in this material. The incommensurate correlations reflect the electronic and lattice effects that appear in the long-range ordered virgin state. A different type of an x-ray-induced transition occurs in Zn-doped CuIr\textsubscript{2}S\textsubscript{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

Filtration X-ray Microscopy for Study of Medium-Range

University of Massachusetts, Amherst, Massachusetts.
Many X-ray techniques exist to probe long- and short-range order in matter, in particular 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-bearing solid-amorphous morphologies, we have developed fluctuation x-ray microscopy (FXM). This novel approach offers quantitative insight into medium-range correlations in materials at nanometer and larger length scales. The FXM examines spatially resolved speckle patterns from coherent x-ray microscopy. 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 polycrystalline domain 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 the use of FXM to measure the 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 a large volume is representative of the bulk. We have applied this technique to investigate the phase transformation in bulk metallic glass. Our data on Zr52,Cu17,Al14,Sn10 showed, for the first time, that the phase transformation in bulk metallic glass proceeds in a stepwise manner, with distinctively different kinetic behaviors. Nanostructured 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 scattering 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-AC05-000R22725 with UT-Battelle, LLC. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Basic Energy Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-31-109-Eng-38. References [1] X.-L. Wang et al., Phys. Rev. Lett. 91, 265501 (2003) 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 patterns from these macroscopic structures give 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 onedimensional rope lattice. We use this approach to select 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 span from super-acid suspensions exhibit mosaic spread as narrow as 31'. 26 Tesla-aligned films exhibit an out-of-plane mosaic of 27'. These results are the best values reported for nanotube films. X-ray scattering is also used to study C60 filled single-walled carbon nanotube (fullerene peapod) films, which has no in-plane preferred orientation. Here, the finite out-of-plane mosaic enables quantitative scattering of one-dimensional diffraction (chains of C60 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.). 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 shape is very promising. 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 films were synthesized via the simultaneous reduction of Pt(acac)2 and thermal decomposition of Co(CO)5 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 mean 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 microscope (TEM) data will be presented revealing the inner atomic structure of the nanoparticles. The preparation and investigation of ordered arrays of nanoparticles...
developed a scanning, polychromatic x-ray scattering technique with submicron spatial resolution on the UNICAT beamline (sector 34) at the Advanced Light Source. In this technique, incident x-rays (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 information on the crystal structure, especially 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 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 samples during 3D 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 Magid1,2, E. T. Lilodden1, N. T. Tumura1, J. Florando4, D. Luslila3, R. Barabash3 and J. W. Morgan3, 1Department of Materials Science and Engineering, University of California-Berkeley, Berkeley, California; 2Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California; 3Advanced Light Source, Lawrence Berkeley National 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 deformation and slip path in a single slip result in carefully oriented samples. The high brilliance x-ray microdiffraction source at the Advanced Light Source (Lawrence Berkeley National Lab) and the micron resolution of the focusing optics allow for mapping of x-ray 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 Laves phase "streaming", which indicates localized rotations in the lattice. These may represent an accumulation of same-sign dislocations (so-called geometrically necessary dislocations).

Theoretical modeling of the diffraction response for various slip systems is proposed, and compared to experimental data. Preliminary results include orientation maps from a highly strained Ti bicrystal and a less highly strained Mo single crystal. The orientation maps of the bicrystal indicate a cell-like structure of dense dislocation walls. This deformation behavior is consistent with previous OIM studies of the Mo single crystal. The results are being used as a proof-of-principle test to understand the more complicated dislocation structures of the Mo single crystal.

2:00 PM Q7.3
In situ Neutron Diffraction Studies of Carbid-Matrix Interactions of Haynes® 230 Nickel Based Superalloy, Tarik A. Salch1,2, Bjorn Claussen, Hahn Cho1,2, Don W. Brown2, Raymond A. Buchanan1, Peter K. Liaw1 and Dwaine L. Klarstrom1, 1Materials Science Engineering, University of Tennessee-Knoxville, Tennessee; 2Los Alamos National Laboratory, Los Alamos, New Mexico; 3Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 4Haynes International, Kokomo, Indiana.

Haynes 230 is a solid solution strengthened, face centered cubic (FCC), nickel base superalloy, with a small percentage of semi-coherent FCC carbides. This alloy is known to exhibit stress-induced transformation and compression anomaly revealed in the behavior of different crystallographic directions under in situ loading. This is 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 Los Alamos Neutron Science Center (LANSE) 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 plastic deformation during loading. Even at room temperature, and even at compressive strain, the carbides began load sharing at the macroscopic yield point. After this point the bulk of the internal elastic strain was carried in the carbide phase. Upon unloading, the residual strains in the carbide phase were an order of magnitude greater than in the matrix. Theoretical modeling to predict the load-sharing behavior of carbides will be attempted. The present work is supported by the National Science Foundation (NSF), the Interdisciplinary Graduate Education and Research Training (IGERT) Program, under DGE-9987548, and the International Materials Institute (IMI) Program under DMR-0231320, and the Combined Research-Curriculum Development (CRCD) Program, under ECC-9527527 and ECC-0095112, with D. P. L. and L. S. Goldberg, L. Clesser, C. Huber and Ms. P. Moats as contra monitors.

2:15 PM Q7.4
In-situ Neutron Diffraction Study of Strain-Induced Martensite Formation and Its Deformation Behavior at a Cryogenic Temperature, Kyungtao Ko1, James J. Wall2, Donald W. Brown3, Sven C. Vogel7, Mark A. M. Bourke7 and Hahn Cho1,2, 1Materials Science and Engineering, University of Tennessee, Knoxville, 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 308, 298, and 208K. X-ray microdiffraction analysis provides bulk measurements of the evolution of phase fractions, texture, and lattice strains during the austenite (fcc) to martensite (bct) 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 293K. However, at 308K, 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-formed martensite phase at 208K is consistent with previous 208K and 298K neutron diffraction studies that show significant load re-distribution from the austenite to martensite phase above 600MPa. The results provide microstructural 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 Cho1,2, Donald W. Brown3 and Mark A. M. Bourke7, 1Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 2Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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 slidinginitiated by the grain boundary stress rate during the creep compared to the quasi-static testing.

5:45 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. Bourke7, 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.
Sven C. Vogel1, David F. Teter1, Daniel J. Thoma1, L. Cate Brinson2, Xiugie Guo3, Raj Vaidyanathan4 and Chandra Rathi3,1
1Mater Data Systems, Advanced Photon Source, Argonne National Lab, L. 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 inherent low density and the cost associated with utilizing at apatition neuron 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 and, copper-zinc-manganese-iron, 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 the total macroscopic deformation and the local 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 inypo+ Si is caused by multiplication mechanism in MD nucleation, eventually enabling the strain field of MD to extend to the top surface of the epitaxial layer.

**4:00 PM Q7.9**

**Microstructure of Cross-Hatch Patterns in p/p+ Si(001) by White Beam Diffraction Microscopy and X-ray Tomography.** J. M. S. I. Setagaya-ku, Tokyo, Japan; 2Institute for Solid State Physics (ISSP), the University of Tokyo, Kashiwa, 3Institute of Materials Science and Technology, Setagaya-ku, Tokyo, Japan; 4Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan; 5Musashi Institute of Technology, Setagaya-ku, Tokyo, Japan.

We investigated the misfit dislocation (MD) nucleation and the dislocation morphology in lightly boron-doped Si(001) layers (200 ppb) on heavily boron-doped Si(001) wafer (0.015 at%) using white beam diffraction microscopy (WBDM) and high resolution x-ray diffraction microscopy (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 <110> 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 inypo+ 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.
fields near crystal surfaces, and applied it to a Si(001) wafer whose surface is covered with a thermal oxide layer. It was revealed that there is a small strain field distributing over mesoscopic-range depth (up to several hundred of nm) under the SiO\(_2\)/Si interface and having a static fluctuation in lateral direction. The PSXD technique is an application of a phenomenon, modulation of the intensity of the crystal-truncation-rod (CTR) scattering under an excitation of a Bragg reflection [1-3], which is an interaction between a two-dimensionally diffracted wave (CTR scattering) and a three-dimensionally diffracted (Bragg reflection) wave. An example will be demonstrated in the case of a Si(001) wafer covered with a thermal oxide layer. The experiment was carried out at BL09XU in SPring-8 in Japan. It was shown that the modulation profile can be characterized by two parameters: the phase shift, which represents the dip or peak position of the modulation profile, and the visibility. Both the phase shift and visibility obtained experimentally were different from those of an ideal perfect crystal. An illustration of the strain field under the SiO\(_2\)/Si(001) interface which can explain the experimentally obtained modulation profile will be shown. The phase shift can be simply interpreted into the sum of displacements of atomic planes under the interface projected onto the direction perpendicular to the 004 plane (-0.16 Å in the case of the example). On the other hand the visibility indicates that the total displacement has a static fluctuation of at least ±0.13 Å in the direction parallel to the interface. The features revealed by the PSXD technique are expected to provide a new window to understand the oxidation mechanism of Si surface. References [1] W. Yashiro, K. Sumitani, T. Takahashi, Y. Yoda, and K. Miki, Surf. Sci. 550, 93 (2004). [2] T. Takahashi and S. 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 Iqbal\(^1\), N. H. van Dijk\(^1\), S. E. Offerman\(^1,3\), M. More\(^2\), L. Katgerman\(^3\) and G. J. Kearley\(^1\), \(^1\)NM, Interfaculty Reactor Institute, TU Delft, Delft, Netherlands; \(^2\)Materials Science/ID11, ESRF, Grenoble, France; \(^3\)Laboratory for Materials Science, TU Delft, Delft, Netherlands.

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