SYMPOSIUM R
Applications of Synchrotron Radiation Techniques to Materials Science

November 29 – December 3, 1999

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Symposium Support
†Blake Industries, Inc.
Lawrence Livermore National Laboratory, (C&MS Dept)
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National Synchrotron Radiation Source (NSLS) at
Brookhaven National Laboratory
†Physical Electronics
†1999 Fall Exhibitor

Proceedings published as Volume 590
of the Materials Research Society
Symposium Proceedings Series.
2:00 PM R1.1

CHARGE TRANSFER AND LOCAL STRUCTURE IN THERMOELECTRIC GERMANIUM CLATHRATES

Andres E.C. Palmqvist, Chalmers Univ. of Technology, Dept. of Applied Surface Chemistry, Göteborg, Sweden; Bo B. Iversen, Univ. of Aarhus, Dept. of Chemistry, Denmark; Lars Parenlid, Univ. of Aarhus, Dept. of Chemistry, Denmark; George Nolan, Marlow Industries Inc., Dallas, TX; Dan Bryon, Susan Lattimer, Galen D. Stucky, Univ. of California, Dept. of Chemistry, Santa Barbara, CA.

Germanium clathrates are semiconducting or metallic host/guest materials that recently have gained attention as potential highly efficient thermoelectric materials. The structure of these clathrates consists of two different types of cages, formed by host atoms from groups III and IV, and filled withGuest atoms of groups I or II. We have performed x-ray absorption studies (XANES and EXAFS) on a series of germanium clathrates to quantify the charge transfer between the host and the guest atoms, and to investigate their local structure. The degree of charge donation between the guest atom and the framework atoms is important for the magnitude of several of the physical properties of these materials and was found to depend on the composition of the clathrate. In a SrGa2Ge5O16 clathrate Sr gives its K-edge only slightly higher than that of strontium metal and ca. 7 eV lower than Sr in strontium hydroxide, indicating a very low degree of charge transfer from strontium to the host atoms in the clathrate. The germanium and gallium K-edges of the clathrates are close to those of the elemental and gallium nitrides. The real part of the dielectric constant ε(0) below those of the Ge(IV) and Ga(III) oxides, in agreement with a low degree of charge transfer to the host.

2:15 PM R1.2

BAND MAPPING OF SINGLE CRYSTAL MOLYBDENUM DISULFIDE T. van Baaren, Lawrence Livermore National Laboratory, Livermore, CA; G. Hirt, University of California at Davis, Davis, CA; C. Bostedt, N. Franco, J. E. Klepeis, L. J. Terminello, Lawrence Livermore National Laboratory, Livermore, CA; T. J. Tersoff, Los Alamos National Laboratory, Los Alamos, NM, J. R. Lince, Materials Science & Technology Center, The Aerospace Corporation, El Segundo, CA.

All MoS2 (0002) single crystals investigated in this study were in the form of the natural mineral molybdenite, obtained from Woud's Natural Science establishment. A clean well-oriented surface of MoS2 (0002) was obtained by cleavage the top layers immediately before transfer into the UHV system followed by short annealing at 600°C. The valence electron structure of single crystal MoS2 was measured by x-ray absorption near edge structure (XANES) using a synchrotron based, angle resolved photoemission using an imaging photoelectron spectrometer at beamline 8.0.0 of the Advanced Light Source. Photoelectron angular distribution images at a fixed kinetic energy were extracted for a variety of photon energies. These images represent constant-energy contours in the MoS2 band structure. A set of such images can be assembled into a complete band structure of MoS2. The constant energy contours are compared with band maps calculated with density functional theory (DFT). We observe the valence band maximum (VBM) to be at the Gamma point with the appearance of features at the K-point 0.06 eV below the VBM. Using the experimental geometry that is reported in the literature the LDA calculations show the K-point features to be 1.1 eV below the VBM. Starting with the experimental geometry we have minimized the total energy by allowing the Mo-S bond length to relax, while holding the a- and c-lattice parameters at their experimental values. The minimum energy occurs when the bond relaxes outwards with a 1.3% increase in the bond length relative to the experimental value. The K-point features corresponding to this relaxed geometry are only 0.7 eV below the VBM, much better agreement with experiment. The experimental bandwidth is 7.9 eV, compared to the value of 7.0 eV obtained in the calculations. The calculations indicate significant band dispersion along the direction perpendicular to the planes. The work is supported by Grants DOE and NSF, Materials Sciences under contract W-7405ENG-48, LANL. C. Bostedt acknowledges fellowship from the German Academic Exchange Service DAAD, N. Franco by the Spanish education and culture office.

2:30 PM R1.3

X-RAY EXTINCTION OF DX CENTERS IN AL, Ga As

Yeong-Ah Soh, G. Aeppli, NIC Research Institute, Princeton, NJ.

ED. Isaac, Recent Technologies, Murray Hill, NJ; A. Penfold, Brookhaven National Laboratory, Upton, NY; Frank M. Zimmermann, Rutgers University, Dept. of Physics and Laboratory for Surface Modification, Piscataway, NJ.

Si dopants in Al-As As act as deep donor levels (DX centers) when x > 0.22. These DX centers can be photoexcited to a metastable state and become shallow donors. In this work, we report on the first use of X-rays to excite the DX centers into their shallow donor state, monitored by measuring the resulting persistent photoconductivity. The energy dependence of the photocurrent closely follows the X-ray detected X-ray fluorescence, indicating that X-ray photoexcitation of core holes is an efficient primary excitation step for the excitation of DX centers. However, there is no appreciable difference between the Ga and As X-edges, implying a non-local DX center excitation mechanism. We verified that this non-locality extends over many microns by measuring the photocurrent of a macroscopic sample excited by an X-ray synchrotron.

3:30 PM R1.4

DETERMINATION OF SURFACE ATOM POSITIONS WITH PHOTON ELE rON HOLOGRAPHIC IMAGING G.J. Lapeyre, H. Wu, S.H. Xu, Y. Yang, H. Crugel, M. Keefe, Montana State Univ., Physics Dept., Bozeman, MT.

Angle-resolved core-level photoemission from an atom of interest contains dispersion effects which are a function of emission direction and wave number related to the photon energy. Using the holographic concept the data can be inverted with a Fourier-like transform to obtain a direct space image [1]. As a result direct surface structure determinations without modeling works, achieving a long sought goal. Experimental methods we use require the continuum property of synchrotron radiation. The properties of the technique will be summarized. Experimental rules of thumb for optimal experimental conditions obtained from simulations will be presented. A theoretical model for the rules will be described. Sites for a number of elements have been measured for Si and GaN surfaces at the Wisconsin Synchrotron Radiation Center and the Advanced Light Source in Berkeley. Examples will be shown to show the power of the method. Research supported by ONR DEPSCOR and NSF. [1] Huanhong Wu, G.J. Lapeyre, Phys. Rev. B 51, 14549 (1995)

3:45 PM R1.5

Abstract Withdrawn.
in order to study the in-plane strain relaxation as a function of etching depth. The results are compared with strain calculations based on finite element method. GBE measurements of the microcrack density at 

HASYLAB offer direct information of in-plane strain and also allow for depth-dependent analysis. Both transverse (diffraction vector along q[110]) and longitudinal (parallel q[110]) scans were performed at different incidence angles, i.e., different penetration depth. At q

positions of the respective grazing peaks truncation rod intensities were recorded. Using the data from FEM and taking into account a modified effective reflection factor for the wires pattern the curve fitted on the basis of GBE algorithm agreed well with the experiment. As main result we find a reduced strain relaxation with increasing penetration depth, especially for shallow etched samples.

SESSION R2: SMALL-ANGLE X-RAY SCATTERING AND SURFACE/INTERFACE SCATTERING

TECHNIQUES I

Chair: Dale L. Perry
Tuesday Morning, November 30, 1989
Suffolk (M)

9:00 AM R2.1

ANOMALOUS ULTRA-SMALL-ANGLE X-RAY SCATTERING BY EVOLVING MICROSTRUCTURES DURING TENSILE CREEP

F.R. Jemian, University of Illinois at Urbana-Champaign, Urbana, IL; G.G. Leng, P. Lefaj and S.M. Wiederhorn, NIST, Gaithersburg, MD.

Failure by creep rupture is a principal design limitation in structural components for long-term applications under stress. Silicon nitride is a prime candidate material for structural components in gas turbines because of its excellent high-temperature mechanical properties. However, it has been observed that different formulations of silicon nitride possess very different creep resistance, and the mechanisms by which improved creep resistance can be achieved are of great interest and not yet well-understood. Silicon nitride is a multi-phase material which consists of elongated beta-silicon nitride grains embedded in the secondary phases originating from the additives necessary for sintering. These intergranular secondary phases are known to control the strength, creep and oxidation properties of the material. Thus, knowledge of the evolution of the crystalline secondary-phase particles and the development of creep cavitation during deformation is crucial for understanding the deformation process and for developing better ceramics.

Ultra-small-angle X-ray scattering has been used in the past to provide quantitative information on the size distribution of cavities. However, in the materials of interest in this research, there are also crystalline particles that have nearly the same scattering contrast as the silicon nitride matrix as the cavities, and, furthermore, they are of similar sizes. To determine both the size evolution of the cavities and the crystalline secondary phases, anomalous ultra-small angle X-ray scattering data was acquired near the L1/2 edges of the rare-earth oxide secondary phases. Both (crystal and particle) size distributions were determined as a function of deformation of SN88 and of extremely creep-resistant SN 281.

9:15 AM R2.2

RADIATION EMBRITTLEMENT STUDIES USING ANOMALOUS SMALL-ANGLE X-RAY SCATTERING

Dale E. Alexander, B. Kestel, Argonne National Laboratory, Materials Science Division, Argonne, IL; Peter R. Jemian, University of Illinois at Urbana-Champaign, Urbana, IL; G.R. Odette, D. Klingensmith, D. Grigg, University of California at Santa Barbara, Department of Mechanical and Environmental Engineering, Santa Barbara, CA; S. Seffen, Argonne National Laboratory, Chemistry Division, Argonne, IL.

As nuclear power plants age, understanding radiation-induced materials degradation in reactor components, as well as for regulatory considerations which may include extending reactor operation beyond the originally planned 40 year license period. Radiation embrittlement of the ferritic steel vessel surrounding the core of light water reactors represents a critical degradation phenomenon for consideration in this regard. Small-angle scattering using x-rays provides a beneficial complementary technique to microscopic ones such as electron microscopy for characterizing the very fine embrittlement microstructure. A small-angle X-ray scattering pressure vessel (RPV) materials. With the availability of variable energy synchrotron sources, the technique of anomalous small-angle x-ray scattering (ASAXS) can be applied to extract composition, size distributions, number densities of hardening centers, and, as used, provide important input into mechanistic hardening models used to interpret embrittlement. In this work ASAXS experiments have been performed at the Daresbury Source on a model R-0.9 wt. % C, 1.0 wt. % Mo RPV alloy. The material was characterized in the following forms: as-prepared (i.e., untreated), thermally annealed (540°C, 24 hours), and electron irradiated (10 MeV electrons, 300°C). The evolution of the microstructure and materials properties was examined for damage levels ≤ 10^-7 displacements per atom. ASAXS experiments were performed at photon energies in the vicinity just below each of the alloy constituent elements K-absorption edges. Based on an analysis of the data performed to date, small scattering centers with radii of gyration of 1.4A and 8A were clearly resolved in the annealed and electron irradiated materials, respectively.

Anomalous scattering was observed in the annealed sample in a manner consistent with the generation of dislocation precipitates. This work was supported in part by the US Department of Energy, BES-Materials Sciences, under contract No. W-31-109-ENG-38.

10:00 AM R3.1

IN-SITU STUDIES OF THE PROCESSING OF SOL-GEL PRODUCED A MORPHOUS MATERIALS USING CURVED IMAGINE PLATE XRDS, XANES AND SANS

Dave M. Hopkins, G. M. Menon, Bob Newport, Univ. of Kent at Canterbury, School of Physical Sciences, Canterbury, UK; Mark E. Smith, Graham W. Wallidge, Univ. of Warwick, Dept. of Physics, Coventry, UK; Mark Roberts, Dareby Lab., SRS, Warrington, UK.

We report an extensive series of synchrotron X-ray studies on sol-gel produced mixed oxide materials utilising intrinsically rapid, and in the case of XRD and SANS parallel channel, experimental methods including: time-resolved small angle scattering, using a quadrant detector, to follow the initial stages of agglomeration between the sol and the gel and thereby reveal characteristic length scales associated with the sol-gel process, ii. The use of a curved image plane detector in diffraction, which allows the simultaneous collection of data across a wide range of scattering (2θ = 0° to 120° at θ = 0.7 A) at high count rate, to study heat treatments, iii. X-Ray Absorption Near Edge Structure to explore, in a manner of other techniques, the revealing irreversible nature of network terminating -OH groups at catalytically important sites by following in detail the variation of Ti-O coordination from 4- to 6-fold using distinctive pre-edge features associated with the Ti-K-edge. The samples were all mixed silica and titania binary materials, studied from the polymerisation stage, through to extremely high density calcined solid. Titania content were in the range 0 - 41 mol%, and heat treatments to 1000°C were applied. The results are presented and discussed within the context of existing solid state 23Si and 17O Mossbauer and other spectroscopic data. The project provides a clear example of the efficacy of modern synchrotron methods in condensed matter science when utilised within a materials centred methodology which makes coherent and cogent use of complementary data.

SESSION R3: SMALL-ANGLE X-RAY SCATTERING AND SURFACE/INTERFACE SCATTERING

TECHNIQUES II

Chair: Dale E. Alexander
Tuesday Morning, November 30, 1999
Suffolk (M)

10:15 AM R3.1

ELECTRICAL DOUBLE-LAYER STRUCTURE AT THE RUTILE-WATER INTERFACE WITH X-RAY STANDING WAVES.
P. Fenter1, L. Cheng2, S. Rihs3, M. Machesky3, P. Geissbühler3, M.J. Bedzyk,1,2 and N.C. Sturchio1,3, Argonne National Laboratory, Argonne, IL; Northwestern University, Evanston IL; Illinois State Water Survey, Champaign IL; University of Washington, Seattle WA.

Knowledge of the distribution of ions at the solid-fluid interface is fundamentally important not only for understanding the interfacial properties but also for predicting the biological activity. Although relatively little is directly known about the structure of the electrical double-layer (EDL), particularly through in-situ studies at the mineral-aqueous interface. The current consensus is that the EDL structure consists of both condensed and diffuse layers. While it is generally assumed that the fraction of ions in the condensed layer will increase as the Debye length decreases, this partitioning of double-layer ions between the condensed and diffuse layers has not yet been directly measured. Such behavior will undoubtedly influence the reactivity of the solid surface and therefore is of fundamental importance in understanding the mineral-fluid interface. We use the specific example of the interaction of Sr (43) and Rb (41) ions with the rutile TiO2 (110) surface to demonstrate that x-ray standing waves (XSW) can provide direct insight into the partitioning of ions between the condensed and diffuse components of the EDL. This surface is known to be chemically altered via exposure to the range of pH, and the surface charging behavior of rutile has been extensively studied. Through both in-situ and ex-situ XSW measurements at the Advanced Photon Source, we find that the partitioning of Rb and Sr ions between the condensed and diffuse layers depends sensitively
upon the ion solution concentration. These results also reveal significant differences in both the structure and stability of these alkali and alkaline earth cations adsorbed on a common substrate. This work was supported by the Geosciences Research Program, Office of Basic Energy Sciences (DOE).

10:30 AM R3.2 X-RAY SURFACE SCATTERING STUDIES OF MOLECULAR ORDERING AT LIQUID-LIQUID INTERFACES. Mark L. Schlossman, University of Illinois, Dept. of Physics, Chicago, IL.

In spite of the scientific and technological importance of liquid-liquid interfaces, very little is known about their structure because few experimental techniques are capable of probing order on the molecular length scale at this interface. I will discuss our recent progress in extending the use of x-ray surface scattering to study the molecular ordering at liquid-liquid interfaces. This includes studies of the following systems: (a) structure and phase transitions in a single fluorescent monolayer at the water-air interface; (b) structure at pure water-air interfaces; (c) structure of phospholipid monolayers at the water-2heptane interface; and (d) large interfacial fluctuations at microemulsion oil interfaces (in 3-phase solutions).

11:00 AM R3.3 A SYNCHROTRON X-RAY STUDY OF LUNG SURFACANT SPECIFIC PROTEIN SP-B IN LIPID MONOLAYERS AT THE AIR-FLUID INTERFACE. Kun Tse C. Lee, The University of Chicago, Dept. of Chemistry, Chicago, IL; Jerzy Majewski, Greg S. Smith, Los Alamos National Laboratory, Michael Lupan Jr., Neutron Scattering Center, Los Alamos, NM; Tanya Kuhl, Joseph A. Zandziman, UCSB, Dept of Chemical Engineering, Santa Barbara, CA; Paul B. Hovius, Kristian Kjær, Rice National Laboratory, Dept of Solid State Science, Technical University of Denmark, Michael H. Lipp, MIT, Dept of Chemical Engineering, Cambridge, MA; Alan J. Wiener, M.I.T., Jr. /Drew Medical Center and UCLA, Los Angeles, CA.

We report the first x-ray scattering measurements to determine the effects of SP-B, SP-A, and surfactant protein SP-B, on the structure of palmitic acid (PA) monolayers. In-plane diffraction that the peptide fluidizes the monolayer, but does not affect the packing of the residual ordered phase. This implies that the peptide resides in the disordered phase, and that the ordered phase is essentially pure lipid, in agreement with fluorescence microscopy studies. X-ray reflectivity that the peptide is oriented in the lipid monolayer, on an angle of ~34° relative to the interface, with one end protruding past the hydrophilic region into the fluid phase, and the other end embedded in the hydrophobic region of the monolayer. We have also examined the collapse structures of PA monolayers, and found that monolayers collapse at a higher surface pressure in the presence of the SP-B, but the spacings of the ordered collapse phase seem to be independent of the peptide. The interfacial distances agree well with potential energy calculations of the same system. The quantitative insights afforded by this study lead to a better understanding of the lipid/protein interactions found in lung surfactant systems.

11:15 AM R3.4 STUDY OF THE BURIED INTERFACE BEHAVIOR OF LIQUID CRYSTAL THIN FILMS USING SYNCHROTRON RADIATION AND GRAZING INCIDENCE X-RAY SCATTERING MODE. Yuki Ito, L.J. Martinis-Miranda, Univ. of Maryland, Dept. of Materials and Nuclear Eng., College Park, MD.

We have used the intensity and tunability of a synchrotron x-ray source in order to access the buried interface between a glass substrate and a liquid crystal film. We find that for an energy of 9.4keV, the x-rays can penetrate a 0.22mm substrate. Grazing Incidence X-ray Scattering have been used to study the films as a function of depth and temperature. Our results indicate the presence of both the cholesteric structure and a structure similar to the helical twist-grafted boundary (TGB) phase. Some films have a disordered disordered interface. We will discuss possible applications of this technique in the study of semiconductor devices as well as surfactant film interfaces. This work was supported by NSF Grant No. ECS-9530833 and ECS-9606609. Work at the NSLS is partially supported by the U.S. Department of Energy.

SESSION R4: SPECTROMICROSCOPY & TOPOGRAPHY I
Chair: Paul Fenter
Tuesday Afternoon, November 30, 1999
Suffolk (M)

130 PM R4.1 REAL-TIME CHARACTERIZATION OF BIOGEOCHEMICAL PROCESSES ON SURFACES OF GEOLOGIC MATERIALS BY SR-FTIR SPECTROMICROSCOPY IMAGING. Hsiu-Ying_N. Ho, Louisiana State University, Baton Rouge, LA; Paul J. Scullion, University of New Orleans, Dept of Mechanical Engineering, New Orleans, LA.

An x-ray microprobe beamline was recently developed and commissioned at the Center for Advanced Microstructures and Devices (CAMD), Louisiana State University. It achieves a moderate vertical and horizontal focal spot size of 18.8 μm x 7.0 μm, respectively. The beamline and endstation are designed and optimized to perform (i) spatially-resolved x-ray fluorescence spectroscopy (spectro-microscopy) using the broad intense spectrum of the synchrotron radiation, and (ii) spatially-resolved x-ray absorption spectroscopy (micro-spectroscopy) in the energy region of
2:45 PM R5.4
DIAGONAL LINE MONITORS FOR DEMANDING SYNCHROTRON EXPERIMENTS. P. Bergonzini, D. Thomson, A. Brambilla, C. Mer, B. Guinard, F. Felloni, LETI (CEA • Technologies Avancées) /DEIN/SP, CEA/Saclay, Gif-sur-Yvette, FRANCE.

With the recent advances in user experiments based on synchrotron light sources, accurate control and stable supply of the photon beam have become necessary. This requires permanent X-ray monitors in the low energy range for such an application. Diamond has two distinctive advantages over the other semiconductor detecting materials: its high radiation and temperature hardness allows long term in-situ analysis, and its low atomic number results in a low X-ray absorption cross section. This combination enables thin film photodetectors to be inserted in the beam line causing no intensity perturbation downstream. They enable the monitoring of intensities, position, and beam cross section. In addition, the short carrier lifetimes in diamond allows the precise measurement of sub-nanosecond pulses, with interests in pulse duration monitoring. Monitors are fabricated from diamond polycrystalline films synthesised using the chemical vapour deposition techniques. Thin layers with varying thicknesses from one to a few hundred micrometers can be fabricated and used either as membranes or in self-supporting films in order to form electrical devices for X-ray detection. The first application addresses the semi-transparent low energy beam intensity and position detector manufacturing for demanding experiments such as XAFS on ultra-dilute samples or polarisation dependent X-ray spectroscopy. Highly transparent beam position monitors (BPM) were made that exhibit at 4 keV a position resolution better than 2 μm. Another application led to the fabrication of detectors for monitoring the intensity and temporal distribution of the X-ray pulse tracks generated by synchrotrons (at the ESRF, on 2/3 filling mode, each electron pack being separated by 2.8 ns). They appear as an attractive alternative to highly sophisticated systems such as streak cameras. These devices open new possibilities for diamond towards the fabrication of synchrotron light characterization tools.

SESSION R5: SPECTROSCOPY & TOPOGRAPHY II
Chair: Stuart R. Stock
Tuesday Afternoon, November 30, 1999
Suffolk (M)

3:30 PM R5.1
X-RAY TOPOGRAPHY STUDY OF SURFACE DAMAGE IN SINGLE CRYSTAL SAPPHIRE. David R. Black, Robert S. Polvani and Katherine M. Medicus, NIST, Gaithersburg, MD.

X-ray diffraction topography was used to investigate the relationship between sub-surface damage, non-surface microstructure, and fracture strength in sapphire components. We report here results from a series of modulus of rupture (MOR) bars that were fabricated as part of a proof test for a fabrication process. The strength of the bars was determined by failures in four point bending. The tensile surface of the bars was examined using optical microscopy and non-contacting surface profilometry and found to have good surface finish, with typical RMS roughness of 0.6 μm. No correlation was found between the surface finish and fracture strength. Surface topographs of these bars prior to fracture testing showed that they clearly were of two distinct types. The microstructure of the first type was typical of well polished sapphire, containing individual dislocations and occasional damage from handling. The topographs of the second type showed an oriented microstructure consisting of a pattern of linear features running the length of the bars. We attribute this latter structure to damage induced during fabrication that was not removed by subsequent processing and/or polishing. Separation of the fracture strength data by type showed that the bars with fabrication damage had a strength more than 30% lower than the bars without this damage. These results clearly demonstrate that topography is sensitive to surface damage that can be correlated with fracture strength but cannot readily be observed by traditional optical methods.

3:45 PM R5.2
DISLOCATION MOTION AROUND LOADED NOTCHES IN ICE. SINGLE CRYSTALS. Daniel Cullen, Xiaohong Hu, and Ian Baker, Thayer School of Engineering, Dartmouth College, Hanover, NH.

Microwave tomography has been used to study dislocation behavior around notches in single crystals of ice during in situ deformation as a constant stress-rate. During deformation at 8° C a dislocation deformed zone (DDZ) formed above the notches in a vertical array of dislocations formed below the notch. Modeling the interaction between basal plane dislocation loops and the notch stress field revealed that this DDZ arose from dislocations gliding completely through the specimen. In addition the model was also used to determine basal plane dislocation mobilities, which were then compared to previous work by others. Also, the differences in temperature on dislocation behavior around notches in ice under uniaxial tension were compared with dislocation activity around the notch at -8°C observed to be much greater than the activity at 40°C and -60°C. Acknowledgements: Grant OPP-9526541 from the National Science Foundation and Grant DAAH04-96-1-0041 from the Army Research Office supported this research.

4:00 PM R5.3
KEYS TO THE ENHANCED PERFORMANCE OF MERCURIC IODIDE RADIATION DETECTORS PROVIDED BY DIFFRACTION IMAGING. Bruce Steiner, NIST, Gaithersburg, Lodewijk van den Berg, Constellation Technology, and Uri Lazor, NIST, Gaithersburg, & SRC, Be'er Sheva.

High resolution monochromatic diffraction imaging is playing a central role in guiding the optimization of mercuric iodide radiation detector performance. The electronic transport properties of mercuric iodide in space exceed those of terrestrial crystals; through diffraction imaging this superior property has been traced to specific differences in crystalline regularity. As a result of the knowledge gained from these observations, substantial enhancements in the electronic properties of terrestrial crystals has now been achieved. The models that were developed on the basis of the imaging have been confirmed through the terrestrial fabrication of devices with progressively improved performance. The monochromatic diffraction imaging on terrestrial crystals follows the observations that superior performance is correlated with the avoidance of inclusions, and not yet with enhanced orientational regularity of the lattice. The absence of correlation in monochromatic imaging to be further confirmed at this stage in determining the superior electronic properties of the space crystals than does the absence of gravity loading of the lattice of the hot crystal during its growth. Nevertheless, through particular attention to purification and the achievement of stoichiometry, the effects of convection in terrestrial growth have been mitigated.

Although the performance of both generations of space crystals to date remains superior to the best of those grown on the ground, the difference has been reduced by more than 90%. Evidence for various factors in the control of inclusion formation will be presented, showing progress in the simultaneous achievement of purity and stoichiometry, which proves to be a challenging requirement. Success in reduction in inclusion formation is found to be strongly dependent on details of the crystal growth process and on the morphology of the growing crystal. The progress to date based on diffraction imaging indicates that the electronic properties of terrestrial crystals have not yet been maximized and that they may naturally be superior to those of the superior space crystals grown to date. Advancement along these lines will be facilitated both by the continued guidance from synchrotron science and by further space experimentation.

SESSION R6: X-RAY DIFFRACTION
Chair: Susan M. McCoy and Thomas H. Burell
Wednesday Morning, December 1, 1999
Suffolk (M)

9:00 AM R6.1

Analyses of time resolved structural changes enable an understanding of the interacting interactions that govern the evolution of crystal structures. This knowledge is essential for the intelligent manipulation of processing and chemistry to control composition, microstructure, and ultimately the functional properties. To achieve these goals, a high temperature furnace (up to 1080°C) has been designed specifically for
use with high-energy synchrotron radiation. This furnace design allows for full bulk sampling in a low thermal gradient environment using Debye-Scherrer transmission geometry. Unlike a flat plate geometry, the transmission geometry allows for solid-liquid as well as solid-solid phase transitions to be explored. Sample spinning has been introduced into the design to assure powder averaging and allow for quantitative phase analysis and structural refinement. The use of an insert detector system has allowed powder patterns to be collected with a time resolution on the order of a few seconds. The kinetic of phase transformations are studied by performing Rietveld refinement on multiple spectra collected throughout the transformation process.

Data collected on the cethochonb to rhombohedral transition in SrCO₃ and the tetragonal to cubic transition in the NiTi system will be presented to demonstrate the capabilities for performing quantitative time resolved high temperature powder diffraction.

9:15 AM R6.2
CHARACTERIZATION OF MIXED-METAL OXIDES USING SYNCHROTRON-BASED TIME-RESOLVED X-RAY DIFFRACTION AND X-RAY ABSORPTION SPECTROSCOPY: STRUCTURAL AND ELECTRONIC PROPERTIES IN IRON MOLYBDATES. Jose A. Rodriguez, Jennifer C. Hanson, Steven Chua, Brooke, Brookhaven National Laboratory, Upton, NY, Joaquim J. Brito, Venezuelan Institute of Scientific Research, Caracas, VENEZUELA; Amishit Maiti, Molecular Simulations, Boston, MA.

Investigations at Brookhaven National Laboratory have established the feasibility of conducting sub-minute, time-resolved x-ray diffraction (XRD) experiments under a wide range of temperature and pressure conditions. This important advance results from combining the high intensity of synchrotron radiation with the new parallel data collection devices. Examples of problems studied to date include the kinetics of phase transformations in mono- and bimetallic oxides, the hydrothermal synthesis and thermal dehydroxylation of oxides, the binding of substrates to inhibitors in zeolites, and the sulfidation and reoxidation of catalysts. Results that illustrate the capabilities of time-resolved XRD will be discussed, making emphasis on recent works that deal with phase transitions in a series of mixed-metal oxides (iron molybdates in particular). In general, mixed-metal oxides play a relevant role in many areas of chemistry, physics and materials science. In principle, the combination of two metals in an oxide matrix can produce materials with novel physical and chemical properties that can lead to superior performance in technological applications. The two metals can behave as isolated units that bring their intrinsic properties to the system, or their behavior can be modified due to the effects of metal-metal or metal-oxygen-metal interactions. In this respect, a technique like synchrotron-based x-ray absorption near-edge spectroscopy, XANES, can be very powerful for examining the electronic properties of the metal components in an oxide. For iron molybdates and other mixed-metal oxides, the Mo L₃ and O K-edges in XANES provide direct information about the oxidation state and coordination geometry of Mo.

9:30 AM R6.3
HIGH PRESSURE DIFFRACTION STUDIES OF MATERIALS RELATED TO CUBIC ZrW₂O₈. Cora Lind, Angus P. Wilkinson, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Michael Seidner, Jiuhun H. Chen, SUNY Stony Brook, Center for High Pressure Research, Stony Brook, NY.

Negative thermal expansion (NTE) materials are of considerable scientific and technological interest. Their use in composites may facilitate the control of thermal expansion and allow the attainment of zero expansion. The high pressure behavior of NTE materials is relevant to their application, as the NTE material will experience compression from the surrounding matrix material when used as a filler in a composite. Phase changes that occur under pressure such as those seen in cubic ZrW₂O₈ (transformation to an orthorhombic phase at 2.5 kbar) are undesirable, as the original expansion properties are lost. We have investigated the high pressure behavior of the NTE materials cubic Zr₂M₂O₈ and cubic H₂MoO₄ in a high pressure cell using synchrotron radiation for in situ observation.实验s were carried out at pressures up to 30 kbar at temperatures up to 600°C, with both white and monochromatic radiation. The influence of hydrostatic versus non-hydrostatic pressure was investigated. Non-hydrostatic conditions lead to amorphization at pressures as low as 15 kbar, while the original expansion properties are seen at the same pressures under hydrostatic conditions. When the amorphous materials were heated under pressure, crystallization to a denser monoclinic polymorph was observed. This polymorph is known to be thermodynamically stable in Zr₂M₂O₈ but had not been seen for H₂MoO₄ prior to this work.
micromechanical damage in two-phase Cu-Mo alloys during plastic deformation. Mechanically-loaded, 1.5 mm thick specimen irradiated with a monochromatic beam of 55 keV photons using the Advanced Photon Source (Argonne National Laboratory). Low-index diffraction rings of both phases were recorded with a high-resolution two-dimensional detector. By means of newly developed data processing routines, we could to quantify as a function of applied stress not only the ring distortion (from which the elastic strain can be calculated) but also the ring graininess (which is related to the peak broadening). Based on this information, we characterized the growth and damage process in these alloys in great detail. As compared to conventional neutron methods, the photon transmission technique yields similar precision but at much reduced measurement times. The main sources of experimental errors are identified and strategies to minimize these errors are discussed.

SESSION R7: MICRODIFFRACTION
Chair: Uta Rustet
Wednesday Afternoon, December 1, 1999
Suffolk (M)

1:30 P.M. R7.1
X-RAY MICRODIFFRACTION STUDY OF Cu INTERCONNECTS.
X. Zhang, H. Selik, F. Cerrina, Electrical and Computer Engineering and Center of Nanotechnology, University of Wisconsin-Madison; B. Liu, Z. Cui, P. Biskic, D. Legnini, W. Rodrigues, Advanced Photon Source, Argonne National Laboratory.

Copper has been chosen as the interconnect material to replace Al-based alloys in the next generation. It has lower resistivity and higher electromigration resistance. Many research efforts have been put into this area for the past two decades and will be put into for many years to come. It is very important to study the material properties, especially under electric stressing, to understand its behavior and improve its performance.

Our Copper interconnects were fabricated using lift-off process. A Leica electron beam lithography tool was used to directly write all the patterns. Eight different linewidths were used in this experiment, varied from 5μm to 25μm. The length of all lines was 1mm. An electron beam evaporation was used to deposit Cu(350nm) or Ti(20nm)/Cu(350nmm) films on these wafers. SiN(0.2μm) and SiO(0.4μm) were deposited as a passivation layer using plasma-enhanced chemical vapor deposition at 350°C. All samples were annealed at 450°C for 30 minutes in a N2(90%)/H2(10%) mixture.

The X-ray microdiffraction experiments were conducted at Argonne National Laboratory. The phase zone plate based micro-beam beamline 3ID-D provides the best performance in the world in terms of spatial resolution. We use symmetric reflection geometry for this experiment, therefore, the strain measurement of our experiments are sensitive only to the surface normal direction. The beam spot used in this experiment is about 1μm in vertical direction and 5μm in horizontal direction.

From our experiment, we found Titanium adhesion layer has a significant effect on Copper interconnect microstructures. Without Titanium adhesion layer, the m-deposited Cu shows no texture and has bigger grains. With Titanium adhesion layer, the m-deposited Cu interconnect has better texture and smaller grains. It also has wider strain variation range. The annealing process has a strong impact in terms of microstructures and stress relieve. The annealed sample shows much stronger [111] texture and narrower strain variation. Feature size affects the strain as well. We found less tensile strain in the smaller features than in bigger feature. Measurement was conducted before and after electromigration test. Mass flow from the void to the void pad has been found directly from Copper fluorescence. The X-ray microdiffraction from the void area shows a significant strain variations. Our data shows that the strain becomes compressive around the hillock region, and becomes more tensile around void region. Diffraction from Cu/Ti alloys was also detected around the void area.

1:45 P.M. R7.2
NONDESTRUCTIVE DETERMINATION OF THE DEPTH OF DIFFERENT TEXTURE COMPONENTS IN POLYCRYSTALLINE SAMPLES.
C.P. Patterson II, K.I. Ignatiev, A. Gueviler, J.D. Haase, R. Morano, S.R. Stock, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA; Z.U. Rek, Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, CA.

The surface and the center average textures (microtexture) of plates of many alloys differ substantially, and nondestructive methods for determining the depth of different texture components would be very useful in a number of material applications. This report discusses evaluation of one method based on recording micro-beam transmission Laue patterns as a function of sample-detector separation and on truing the diffracted rays back to their physical origin. Polychromatic synchrotron x-radiation and absorption edge filters are used. Results from sections of Al-Cu 2024-T341 plates are reported, and limitations of this x-ray tracing technique are discussed.

2:00 P.M. R7.3
PLASTIC DEFORMATION, RECRYSTALLIZATION AND INTERNAL STRESSES STUDIED BY A NEW 3D X-RAY MICROSCOPE. D. Juel Jensen, H.F. Poulsen and T. Lorentzen, Materials Research Department, Risø National Laboratory, Roskilde, DENMARK.

With high-energy highly-intense synchrotron radiation it is possible to penetrate deeply into most metallic materials and to focus/collimate the incident and diffracted beam to a small (μm) sized volume in the bulk of a sample. Thereby 3D characterizations at a macrostructural relevant scale become reality. In the first part of the presentation, the experimental set-up is described. In collaboration with ESRF the instrument is presently being assembled and tested in a dedicated hutch at the beamline ID11 at ESRF in Grenoble, France.

In the second part of the presentation new experimental results are used to illustrate the potentials of the technique. Three topics are chosen:

- Plastic deformation: the crystallographic orientations of the grains in a selected volume of an undeformed polycrystalline sample will be characterized using the synchrotron technique. After plastic deformation, the same grains will be identified and their orientation characterized. Because of the knowledge of the initial orientation of each deformed grain this will allow evaluations which have not previously been possible, for example of texture models, active slip-systems and grain-grain interactions.

- Recrystallization: in situ annealing of deformed samples will allow determination of nucleation rates and of growth rates of individual grains. The latter may be studied either by looking at the total increase in intensity from a single grain or by looking directly at the motion of a selected grain boundary segment into the surrounding deformed material.

- Internal stresses: the high spatial resolution is applied to study local stress strain variations in heterogeneous microstructures, primarily composite systems or polycrystalline aggregates. Such investigations, in turn, will allow critical validation of numerical models for both composite materials and polycrystalline plasticity.

2:30 P.M. R7.4
3-D MEASUREMENT OF DEFORMATION MICROSTRUCTURE IN AI(0.2% Mg) USING SUBMICRON RESOLUTION WHITE X-RAY MICROBEAMS. B.C. Larson, N. Tanaka, J.-S. Chung, G.B. Ice, Oak Ridge National Laboratory, Oak Ridge, TN, H. Walland, Alcoa Technical Center, Alcoa Center, PA, and W.L. Low, Howard University, Washington, DC.

We have used submicron resolution white x-ray microbeams on the MJATT-CAT beamline at the Advanced Photon Source to investigate this three-dimensional deformation microstructure in a 20% strain plane compressed Al(0.2% Mg) tri-crystal. K-B mirrors were used to focus the white beam of the MJATT-CAT undulator to a 0.7 x 0.7 μm² beam, which was scanned over bi- and tri-crystal regions near the triple junction of this tri-crystal. White beam Laue photographs were collected using a CCD x-ray detector. Depth resolution along the x-ray microbeam of 3.3 microns was achieved by triangulation back to the diffraction source point through the use of CCD pictures taken at series of 11 different distances, varying from 25 - 50 mm from the sample. Computer indexing of the deformation cell structure in the bi-crystal region provided orientation of individual grains to 0.01 degrees, making possible detailed measurements of the rotation axes between individual cells. The techniques used in making the measurements and the analyses, and the potential of white microbeam x-rays for the investigation of materials microstructure and macrostructural evolution will be demonstrated.

* Research sponsored by the U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. N. Tanaka and J.-S. Chung are supported by the Office of Basic Research, DOE. The MJATT project is cooperatively supported by ORNL and OHISE. The x-ray measurements were performed on the MJATT-CAT beam line at the APS. The APS is supported by the DOE Office of Energy Research under contract W-31-1-ENG-38.

2:45 P.M. R7.5
An experimental station dedicated to the local structural characterization of bulk materials has been set-up at the ESRF. High energy synchrotron radiation (4k-90 keV) is employed providing the necessary penetration power to investigate several millimeter thick samples of technologically relevant metals or ceramics. The local gauge volume is defined by a combination of micro-focusing, broad band monochromators and the position sensitive detection systems behind the sample. We are aiming for a 3-dimensional gauge volume of $5\times5\times50$ micrometers whereas a resolution down to 1 micrometer can be achieved in 1 dimension. The technique is non-destructive and allows for in situ and in situ achievements of thermomechanical stressing. This presentation focuses on the measurement of the local strain/stress state. The development of a strain scanner with micron sized gauge volume is described by experimental studies including metal matrix composites, thick coatings, shot-peened surfaces and tension and torsion deformation. Difficulties that a local strain scanning technique has to deal with are: the definition of the gauge length along the incident beam without bringing optical elements too close to the transmission limit from the specimen. Nevertheless, the case fast data acquisition by multiplexing and the positional stability under sample rotations. Experimental solutions to these problems are presented and future developments are anticipated.

SESSION R8: MICRO-TOMOGRAPHY / PHASE CONTRAST
Chair: Stuart R. Stock
Wednesday Afternoon, December 1, 1999
Suffolk (M)

3:30 P.M. R8.1
APPLICATION OF SYNCHROTRON RADIATION TO IN VIVO MICRO-TOMOGRAPHY: THE OXV HAT MODEL OF OSTEOPOROSIS. J.H. Kimney, University of California, San Francisco, CA; Lawrence Livermore National Laboratory, Livermore, CA; and N.E. Lane, University of California, San Francisco, CA.

Trabecular bone is a highly porous structure consisting of interconnected rods and plates. It is a significant fraction of the total bone mass in the vertebral bodies and the femoral neck, anatomic sites normally associated with osteoporotic fracture. The high intensity and the rotation of synchrotron radiation make it an ideal source for microtomographic imaging of trabecular bone. We have successfully used synchrotron radiation at the Stanford Synchrotron Radiation Laboratory to image the trabecular bone structure in decalcified rat, in vivo, thus providing serial data on the earliest architectural changes that occur with estrogen loss. Over a thousand scans have now been performed on live animals without ill effect. Results from the in vivo studies demonstrate that one of the earliest manifestations of estrogen loss, in addition to a decrease in the amount of trabecular bone, is decreased connectivity of the trabecular lattice. We observed that estrogen replacement therapy, when initiated soon after significant changes have occurred, restored bone mass to baseline levels but did not recover the trabecular connectivity. Finite element calculations based on the three dimensional images of the trabecular bone indicate that recovery of connectivity is necessary for recovery of bone strength unless the remaining trabeculae can be thickened back to baseline values.

We observe such thickening in the proximal tibia with pulsed doses of estrogen; however, the behavior in the vertebral bodies does not show this estrogen response. These results have important implications for the treatment and prevention of osteoporosis. Work supported by the National Institutes of Health (ROI-AR 43052), and by the US DOE Basic Energy Sciences Division which supports SRBL.

3:45 P.M. R8.2
ATTENUATION- AND PHASE-CONTRAST MICRO-TOMOGRAPHY USING SYNCHROTRON RADIATION FOR THE 3-D M. INVESTIGATION OF SPECIMENS CONSISTING OF WEAKLY AND NORMALLY ABSORBING ELEMENTS. Felix Beckmann, Hamburger Synchrotronstrahlungsabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, GERMANY; Ulrich Hone, Institute of Physics, University of Dortmund, GERMANY.

Microtomography using synchrotron radiation has become a valuable tool for the 3-dim. investigation of samples in the fields of e.g. medicine, biology, and materials science. Attenuation as well as contrast at photon energies in the range of 8 to 25 keV and phase contrast at photon energies of 12 keV and 20 keV at beamline BW2 of HASYLAB at DESY, Germany, a large number of samples are investigated. The advantages and limits of the two different contrast mechanisms are presented. Furthermore enhancements for the investigation of larger specimens by applying scanning techniques using a 2-dim. X-ray detector and new developments in high-energy microtomography using synchrotron radiation in the energy range of 60 to 100 keV are described. Using phase contrast at 70 keV it is demonstrated that the 3-dim. structure of weakly and normal absorbing material can be simultaneously revealed.

4:00 P.M. R8.3
X-RAY PHASE CONTRAST IMAGING STUDY OF ACTIVATED CARBON/ CARBON COMPOSITE. Kenji Kobayashi, Kochi Iruma, Hidekazu Kimura, Sigeru Kimura, Tomonori Ohara, NEC Corporation, Fundamental Research Laboratories, Tsukuba, JAPAN; Tatsuki Shito, Yukari Kita, Fundamental Research Laboratories, NEC Corporation, Livermore, Livermore, Kanagawa, Takaki, Takashi Hori, Yasushi Kigoshima, Junji Misono, Fac. of Science, Himeji Inst. of Tech., Akkai, JAPAN.

X-ray phase contrast is a new imaging method based on the refraction of x-rays. This method is a useful tool for weakly absorbing materials such as biological samples because the refraction is more sensitive than the absorption for the light atomic elements. However, this method is not often applicable for the electronic devices because of the low spatial resolution. In this report we present the x-ray phase contrast measurements with high spatial resolution. The transmitted x-rays from a sample were expanded by using analyzer crystals with asymmetric Bragg reflection (asymmetric factor h). Since the analyzer crystals were placed in (+-) arrangements in both vertical and horizontal directions, the total magnification factor became $1/b^2$ for each direction. The x-ray phase contrast measurements were performed at Hyogo-juk line 210XU in SPring-8. The x-rays emitted from the 8-figure undulator were monochromatized to $\lambda=0.83\ \AA$ by using the Si[111] double crystal monochromator. The typical beam size was 1x1 mm$^2$ at the position of the sample. By using the Si analyzer crystals with a surface plane $<100>$ and a diffraction plane $<511>$, the transmitted x-rays were magnified about 23 times. The spatial resolution was about 2 $\mu$m. We applied this method to activate carbon composites which are composed of single layers of electric double-layer capacitors (EDLC) so that it was possible to observe the phase contrast corresponding to the carbon particle with $10 \mu$m.

4:15 P.M. R8.4
SYNCHROTRON X-RAY SCATTERING STUDY OF THE OXIDATION OF AIN/SAPPHIRE(0001) FILMS. Hyon Chol Kwon, Seon Hee Seo, and Do Young Noh, Korea Research Institute of Science and Technology, Dept of Materials Science and Engineering, Kwangju, KOREA.

The structural transformation of AIN/Sapphire(0001) thin films into epitaxial AION thin films during thermal oxidation was studied by in situ synchrotron x-ray scattering measurements. The formation of AION started at the AIN films were annealed at ~750°C, and completed at 950°C. The film surface roughened gradually as AION was formed. The AION films have cubic spinel structure with the $<111>$ direction parallel to the substrate normal, sapphire $<0001>$ orientation. The in-plane crystalline axis was rotated by 30°, resulting AION $<111>$/sapphire $<110>$ and AION $<110>$/sapphire $<112>$ orientation. The lattice constants of AION changed from 5.924 to 8.102 A as the oxidation proceeds at 950°C, which is attributed to the change of oxygen content. The in-plane (surface normal) domain size of AION films also increased from 10 to 30 A during the oxidation, respectively. This suggests that the nano-size AION crystalline was initially formed, and the grain-growth progressed gradually.

4:30 P.M. R8.5
STRUCTURE OF THE NEAR-SURFACE WAVELAYER FORMED BY TITANIUM DIFFUSION IN LITHIUM NIOBATE. Yusuke Aramihara, Emile Zakoutniko, Technical-IT, Dept. of Materials Engineering, Haffen, TISAFL, Wolfgang Stier, Til-Henning Metzger, Johann Pohl, Sektoon Physik, Ludwig-Maximilians University, Munich, GERMANY.

Ti diffusion at 1800°C in an oxygen environment is used in fabricating lithium niobate (LiNbO$_3$) based opticoelectronic devices in order to increase the refractive index of the near-surface LiNbO$_3$ layer. An optical barrier to the propagation of light from the crystal bulk arises from reflection of the Li or Nb cations by Ti ions and related changes in structural parameters and strain levels. In this paper the phase formation processes, accompanying high-temperature Ti-diffusion in thin waveguide layers of LiNbO$_3$ and their influence on the structural characteristics of the LiNbO$_3$ matrix, were studied by grazing-incidence x-ray diffraction (GID) on synchrotron beamlines, high-resolution x-ray diffraction (HRXRD) and complementary techniques, such as transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS). In combination with TEM helped us to follow the development and temporal decay of a rutile-like phase, [Li$_5$O$_{10}$Nb$_2$O$_{32}$]$_{2-}$ [TiO$_2$]$_n$, as well as its orientation relations to the matrix. A new solid state reaction is proposed which leads to the mechanism of phase transformation and role of cation replacements. By comparison of
R9.1 A NEW TRIPLET CRYSTAL DIFFRACTOMETER FOR HIGH ENERGY SYNCHROTRON RADIATION AT ARGONNE NATIONAL LABORATORY. R. U. Rees, Materials Science Division at Argonne National Laboratory and Northern Illinois University, M. A. Bonn, Materials Science Division at Argonne National Laboratory. J. Schlenker, Materials Science Division at Argonne National Laboratory, Strahlungslabor (HASYLAB) at DESY, GERMANY, P. M. Mares, Materials Science Division at Argonne National Laboratory and University of Illinois at Chicago, Chicago, IL.

The new triple crystal diffractometer built at the Advanced Photon Source (APS) at Argonne National Laboratory will be introduced here. It is a new triple crystal magnetic wiggler with a critical energy of 32.5keV. This is the first soft x-ray diffractometer for photon energies above 60 keV in the US. In contrast to the other two diffractometers at HASYLAB (Germany) and ESRF (France) this one is operated with a vertical scattering plane, while a horizontally scattering pre-monochromator beamline. This allows one to take full advantage of the small vertical beam divergence and offers one the possibility of focusing the beam horizontally without limiting the instrumental resolution. High energy photon diffraction is characterized by very high q-space resolution combined with high penetration depth. It offers the opportunity to study samples sub-millimeter thick and takes advantage of the high resolution and intensity of x-ray diffractometers installed at modern synchrotrons. Such an instrument enables to probe true bulk properties, local structures and precose lattice parameters. Because of the highly collimated resolution function detailed studies of even weak charge densities without limitation to a scattering surface are possible. The diffractometer and first test results will be presented here showing the overall performance of the instrument. Acknowledgment: Work at Argonne National Laboratory is sponsored by the Office of Basic Energy Science, Division of Materials Sciences, under contract W-31-109-EN-38 and the State of Illinois under HECA.

R9.2 STRUCTURAL CHARACTERIZATIONS USING SYNCHROTRON RADIATION OF OXIDE FILMS AND MULTILAYERS GROWN BY MOCVD. C. Delapierre, J. Lindner, M. Roisin, F. Weiss, J.P. Scineuse, Laboratoire des Matériaux et du Génie Physique, ESPG, UMR CNRS, St. Martin d'Hères, FRANCE, J.L. Hodeau, J.F. Berr, Laboratoire de Cristallographie, CNRS, Grenoble, France; E. Doorive, European Synchrotron Radiation Facility, Grenoble, FRANCE.

Synchrotron radiation at the European Synchrotron Radiation Facility (Grenoble - France) has been used to characterize oxide thin films and multilayers grown by metalorganic chemical vapor deposition (MOCVD). The investigated heterostructures were: laneyate manganite La0.67MnO3 film and superlattices of (Bi2TeO4/SrTiO3)15 and (La0.67Sr0.33MnO3/SrTiO3)15. The reflectometry measurements were performed on the beamline (BM16 beam line) to get information on the quality of the film/substrate and film/film interfaces of the substrates. The experimental data were compared to simulated spectra. For La0.67MnO3 film deposited on SrTiO3, the roughness is about 0.8 nm (about two unit cells) for a total thickness of 100 nm. For (Bi2TeO4/SrTiO3)15, multilayers, the roughness is found to be less than 1 nm. Anomalous diffraction was performed on superlattices (Bi2TeO4/SrTiO3)15 and (La0.67Sr0.33MnO3/SrTiO3)15 on CRG-2D2A beam line. This beam line is equipped with seven circle goniometer. The multilayers are oriented with the 001 direction perpendicular to the substrate plane. Only the 001 diffraction peaks were recorded, up to the 008 one. Four different incident wavelengths, below and at the absorption edge of strontium (16.000 keV, 16.092 keV, 16.126 keV, 16.129 keV) were used for each peak. A series of peaks for both types of heterostructures indicate the good coherence over the whole stacking. For the (Bi2TeO4/SrTiO3)15 systems, the diffraction peaks are perfectly well resolved even for the highest order (008 peak), showing an excellent epitaxial quality. Such results indicate the high quality of the layers, the high temperature preparation and the good adhesive properties of the substrate. The presence of superlattices in the mixed phase region (15-30%) was evidenced by the appearance of the 001 Bragg reflections.
We report time-resolved, synchrotron small angle X-ray scattering (SAXS) studies of crystallization and subsequent melting in high performance polymers treated by two-stage melt crystallization. The purpose is to study formation of secondary crystal populations under conditions where geometry has been restricted by prior crystal growth. Poly(ethylene terephthalate), PEK, and its blends with 20-30% amorphous poly(etherimide), PEI, were crystallized at T1, then further crystallized at T2. Holding times at T1 and T2 were varied, and both treatments T1<T2 or T1>T2 were examined. Real-time SAXS during the two-stage treatments shows time-dependent intensity changes correlated with the formation of lamellar structures having characteristic peaks of perfection. These results are supported by thermal analysis using differential scanning calorimetry, which shows dual or triple melting endotherms, depending upon whether T1<T2 or T1>T2. Analysis of the SAXS one-dimensional electron density correlation function allows determination of the long spacing, SAXS inversions and further crystallization is strongly affected by the addition of PEI to PEK, and also change systematically during thermal treatment. Results are consistent with an intercalation reaction for PEI. We find no evidence for formation of large amorphous pockets for either treatment scheme.

GROWTH TWINNIN IN Yb2Y1−xAlx(BO3)3 AND Nd2Gdx−1Alx(BO3)3 CRYSTALS OBSERVED BY WHITE-BEAM SYNCHROTRON RADIATION TOPOGRAPHY. X. Li, H. Bao, J. Yang, A. Li, J. Huang, Z. Guo, T. Xiao, J. Wei and Y. Liu, School of Physics, University of Jinan, JIN. P. CHINA.

Growth twins in Yb2Y1−xAlx(BO3)3 and Nd2Gdx−1Alx(BO3)3 crystals were observed by white-beam synchrotron radiation topography combined with chemical etching method. It has been found that the growth twins in Yb2Y1−xAlx(BO3)3 are of inversion type in which two twinned pairs have the central inversion relationship, whereas the growth twins in Nd2Gdx−1Alx(BO3)3 crystals are of 180° rotation type in which the twofold symmetric operation axis is parallel to the [001] axis. The inversion twins in Yb2Y1−xAlx(BO3)3 crystals are visible in x-ray topography not by ‘domain contrast’ but by ‘boundary contrast’ stemming from the kinematically unfixed twin boundaries. However, the rotation twin in Nd2Gdx−1Alx(BO3)3 often show twin film does not show twin contrast in x-ray topography originating from the different structure features between two twinned pairs. In addition, the formation mechanisms of twins are discussed.

LOCAL STRUCTURE PARAMETERS OF THIN FILMS AND ORDERED GE NANOCALLSTERS IN 5x MATRIX BY XAFS. N. V. Bash, J. A. Voss, V. K. Khilaidze, J. T. Lappas, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; N. P. Steppina, A. I. Nikiforov, Institute of Semiconductors Physics SB RAS, Novosibirsk, RUSSIA.

The local microstructure parameters of Ge were determined in Ge films on Si(001) produced by molecular beam epitaxy process. Due to the 4% lattice constant and interatomic distances of Ge, strain evolving during growth of Ge films on Si(001) causes a series of critical morphological and some local spatial structure changes. Spatial parameters of Ge atoms surrounding were determined from Ge K EXAFS data using EXCURV 95 program. XAFS measurements were performed at the VEPP-3 storage ring at the Budker Institute of Nuclear Physics in Novosibirsk. XAFS spectra were measured in surface sensitive mode based on total electron yield detection. The samples positions were kept to provide angles 0° and 90° between the normal of the Si(001) plane and the electron field vector to determine structural parameters anisotropy. Two structures were formed in parallel on two part of Si(001) substrate. Both structure type composed of three Ge/Si bilayers. The first structure of the type contains three pseudo-amorphous 4-monolayer Ge (2D) films, the second structure type contains in addition to the flat critical thickness 4-monolayer Ge films - pyramid-like (3D) islands formed in Stranski-Krastanov growth in order to reduce a high strain energy. This self-organized uniform Ge nanostructures have lateral sizes ~ 1nm and high ~ 1nm. The local microstructure parameters (interatomic distances, Ge coordination numbers and their anisotropy) were linked to nanostructures morphology and adequate mechanisms were suggested and discussed. In particular, it was found that pseudo-amorphous 4-monolayer Ge (2D) films, as it is called, consist of 50% (Ge-Si) solid solution, in contrast with pyramid-like (3D) pure Ge islands formed in Stranski-Krastanov growth.

X-RAY SPECTROSCOPIC STUDY OF THE TRANSFORMATION OF ULTRA-DISPERSED DIAMOND TO CARBON ON PARTICLES A.V. Ostroukh, L.G. Bahabash, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; V.L. Kuometsov, Yu.V. Butenko, A.L. Chavulin, Borekov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA.

At the initial treatment of ultra dispersed diamond (UDD) the onion-like particles consisting of graphene shells are formed. The morphology and size of this particles depend on the method of diamond production and temperature. The samples of carbon particles formed at the different temperature were investigated by X-ray fluorescence spectroscopy.

The surface structure of liquid metals is a subject which provides considerable interest as well as a considerable challenge for theory: the concepts of classical liquids, ideal metallic behavior, and local coordination all play a role in studies so far. The metallic liquid, comprised of disordered, and fast-crystallizing, liquid metals, is governed by complicated interionic interactions which are not addressed by theories of simple liquids. The screened Coulomb potential governing the bulk liquid metal given way to the surface of the van der Waals interactions that prevail in the vapor, giving rise to surface ordering which is not expected for nonmetallic liquids. We present surface x-ray scattering studies of several elemental liquid metals and binary alloys. X-ray reflectivity studies of Hg, Ga and In demonstrate the atomic stratification long predicted to occur at liquid metal surfaces. In the case of liquid metal alloys, we find that surface layering must compete with the formation of surface phases having a more complicated structure. We present results on the wetting transition in Ga-Be, and on the temperature dependent solubility of Au in Hg, the first atomic studies done for these systems. We discuss the application of this technique to in-situ studies of reactions and catalysis at the liquid metal surface.
Measured spectra were compared to the CKα spectra of the initial UDD sample and the nontextured graphite. The CKα spectrum of the on-line plasma preheated at the temperature 1700K was found to considerably differ from the both these spectra and to have the strong intensity in the short-wave region. The interpretation of CKα spectra was performed on the basis of quantum-chemical calculations of series of carbon nuclei using the number of various and kind of the topological defects.

R9.12

High-resolution CKα spectra were obtained for the samples containing carbon cage particles synthesized by the arc-discharge graphite precipitation technique. Inner part of the carbon deposit contains 90% of percent multivertical carbon nanotubes (MWNNT). CKα spectrum of MWNNT is similar to that of polycrystalline graphite. The dependence of the spectral profile on the geometry was investigated using quantum-chemical calculations of the carbon nanotubes fragments with different helical pitch. The spectrum of multivertical particles was found to agree best with the theoretical spectra of zigzag tubes. X-ray emission of textured graphite has the angle dependence, that makes possible to share the alkali and p-electron contribution to the valence band. Yield of fluorescence from the sample of MWNNT was measured for five orientation of the sample relative to the direction of X-ray emission. The difference between CKα spectra of nanotubes is less than that in the case of graphite. CKα intensity in the short-wave spectral region has obvious angle dependence allowing to separate pi- and sigma contributions. The quantum-chemical simulation of density distribution of the sigma and pi-electrons for the carbon nanotubes has good correlation with the X-ray emission experimental data.

R9.13

In Institute of Nuclear Physics the unique one-coordinate detector OB3 for synchrotron radiation (SR), was designed for X-ray diffraction (see V.M.Aulichenko, J. Synchrotron Radiat., 1996, 5, p. 263). The time resolution of this detector for one frame is 1 microsecond. The amount of the frames can be near 1000 with practically zero dead time. The detector has two modifications for XAS and XRF measurements. Now this detector is using at Photon Factory (KEK, Japan), Spring8 (Japan) and VEP3-3 (Russia) at four SR beam lines. The detector was used for the analysis of the fast structural changes during technological processes, such as heating (cooling) with velocity 1000000 deg/sec, electrochemical reactions, solid state reactions, gasless combustion synthesis, photochemical reactions. During experiments at SR beam lines the samples was in reactors with controlled medium (high vacuum, air, gas mixtures, or water solutions) and temperature. With the help of the detector the unique results about behaviour of a crystal lattice was received during a rapid heating (the time of the exited electron gas thermalization was received), about products of the chemical reactions in solids at their initial stage (nucleation process was investigated), about formation and disappearance of intermediate products (new intermediate products was detected), about kinetics of the fast chemical reactions (new information about reactions solid + solid was received), about quasimaterials to - crystal phase transformation (was found that this process is reversible in the short temperature interval).

R9.14
IS IT POSSIBLE TO REALIZE THE X-RAY DIFFRACTION EXPERIMENT WITH PICOSECOND TIME RESOLUTION? Boris Tolechkov, Institute of Solid State Chemistry, Dept of Synchrotron Radiation, Novosibirsk, RUSSIA; Mike Fedotov, Gennady Kulipanov, Pavel Logachev, Nikolay Mezentsev, Sergey Mushnev, Institute of Nuclear Physics, Dept of Accelerators Physics, Novosibirsk, RUSSIA.

For implementation of experiments with a nanosecond time resolution we use fast displacement of a electron beam in the storage ring by electromagnetic chopper (see B. Tolechkov et al., Rev. B, 1996). Moving of the chopper the idea of the nanosecond time resolution experiments, Preprint HEP No 98-28, Novosibirsk, 1999; and the same in the NIM in press). The fast change of orbit electrons results in displacement of a beam of synchrotron radiation. The parallel displacement of synchrotron radiation beam impinges with a speed near 200 km/sec. It allows to conduct scanning by a synchrotron radiation beam on a sample. By establishing after a sample a position sensitive X-ray detectors we receive diffraction patterns with a time resolution equal to time between electrons bunches (250 nsec on VEP3-3 and 5 nsec on VEPP-4 and exposition time 1 nsec and 100 psec respectively).

The described scheme used for research with a nanosecond time resolution of the behavior a crystal structure under external influence. We make the theoretical estimation of the scheme which will allow to execute a beam scanning of synchrotron radiation with speed near 100000 km/sec that will allow to receive a 10 picosecond time resolution (period between frames) and the same exposure time.

SESSION R10: THERMOELECTRIC AND MAGNETIC MATERIALS: X-RAY PHOTOEMISSION, STANDING WAVES AND NUCLEAR RESONANCE SPECTROSCOPY - I
Chair: Susan M. Ming
Thursday Morning, December 2, 1999
Suffolk

09:00 AM R10.1 HIGH-RESOLUTION STRUCTURAL ANALYSIS OF THE Te/Ge(001) SURFACE. Osamu Sakata, Northwestern University, Paul F. Lyman, Univ. of Wisconsin-Milwaukee, Brad P. Tinkham, Don A. Walko, Northwestern University, Michael J. Bedzyk Northwestern University and Argonne National Lab.

Surface structures formed by adsorption of Te on Ge(001) were studied with X-ray standing wave and x-ray scattering measurements. The latter took place at a new soft x-ray chamber/diffractometer in the Advanced Photon Source. At a coverage of 1 ML, Te is adsorbed at the bridge site in a 1×1 arrangement, as expected. However, at 1.5 ML, a new surface structure is formed in which Te-Ge heterodimers make up a n(2×2) surface unit cell. The results help to explain the effectiveness of Te as a surfactant in the epitaxial growth of Ge on Si[001]. **Work supported by the US DOE under contract No W-31-109-ENG-38.**


A new method for microscopically determining the polarity of epitaxial ferroelectric thin films has been developed. The method is based on the weak modulating X-ray standing wave (XSW) field that is excited inside of a single crystal thin film during kinematical Bragg diffraction from that film. In conventional XSW measurements strong dynamically diffraction from a perfect crystal causes both the reflectivity and the visibility (V) of the interference fringes to approach unity. In contrast, the [001] Bragg peak from a 10 nm thick PbTiO3 film has a reflectivity of ca. 10^-4 leading to V \approx 10^{-2}. By using the high x-ray intensity from an undulator synchrotron radiation source, we are able to observe the correspondingly weak modulations in the fluorescence yields from the atoms within the thin film and use this to reliably locate the position of these atoms in the film lattice. We have used the thin-film XSW method to directly determine the domain polarity of as grown PbTiO3 thin films and to observe polarity switching in Pb(Zr0.53Ti0.47)O3 (PZT) capacitors. **Work supported by the US DOE under contract No W-31-109-ENG-38 to ANL, and by the NSF under contact No DMR-9815293, and No DMR-9812472 to the MRC at NU.**

09:30 AM R10.3 INELASTIC NUCLEAR RESONANT SCATTERING STUDIES OF PHONONS IN ALLOYS. Brent Fulgi, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

Nuclear resonant x-ray scattering is usually performed by using the M(5/2) emission. For the past decade, this elastic scattering experiments have been practical to perform with synchrotron radiation. More recently, with the advent of high-resolution monochromators (resolutions at 14 keV of 1 meV or less [1]), it has become possible to perform nuclear resonance scattering accompanied by photon creation and annihilations [2]. The present inelastic experiments are insensitive, in the case of 14 keV of 1 meV internal
conversion x-ray from the sample is detected. The measured inelastic spectra are analyzed to provide a phonon partial density of states of Fe in the sample, using procedures nearly identical to those for inelastic incoherent neutron scattering. The phonon partial DOS is the projection at the 57Fe atom of the phonon polarization intensity. It provides a local viewpoint on how the 57Fe atoms vibrate. We have been unable to extract the resonance scattering amplitudes to study which ions in alloys with various sites of chemical and structural disorder. Our motivation is to understand how the vibrational entropy depends on the state of order in the alloy. Measurements on nanocrystalline 57Fe show a broadening of the phonon DOS at high energies, and an enhancement of modes at low energies [3]. These results are comparable to results from inelastic neutron scattering. Results will also be reported on measurements of coherent disorder effects in partially-ordered and ordered FeAl [4] and PtAl alloys. Chemical order in these alloys was characterized thoroughly by conventional Mossbauer spectroscopy and by x-ray diffractometry. The phonon partial DOS was measured after order was destroyed by disorder during the chemical order, especially in the optical modes. The data support a picture where the phonon partial DOS, and hence the vibrational entropy, of the alloy depends primarily on the chemical environments of the 57Fe atoms. [3] M. Seto, et al., PRL 74, 3828 (1995). W. Sturhahn, et al. PRL 74, 3832 (1995). [4] Fultz, et al., PRL 79, 937 (1997). [4] Fultz, et al., PRL 80, 3040 (1998).

SESSION R11: THERMEOELECTRIC AND MAGNETIC MATERIALS: X-RAY PHOTOEMISSION SPECTROSCOPY AND NUCLEAR RESONANCE SPECTROSCOPY - II

Chair: Dale L. Perry
Thursday Morning, December 2, 1999
Suffolk (M)

10:30 AM R11.1
INTERPLAY OF CHARGE, ORBITAL, AND MAGNETIC ORDER IN Fe3O4, Co2+O2-, Cu, Zn, and V. Zimmermann, D.P. Hall, Doven Gillis, M. Blume, Dept. of Physics, Brookhaven National Laboratory, NY; D. Casu, B. Reimer, Dept. of Physics, Princeton University, NJ; Y. Mukuoki, Photon Factory, Tsukuba, Japan; Y. Tomita, Joint Research Center, Tsukuba, Japan; Y. Tsuchiya, Dept. of Applied Physics, University of Tokyo, Tokyo, Japan.

It has recently been possible to directly observe the charge valence and orbital ordering in magnetic materials through the use of 71 resonant x-ray scattering [1]. The sensitivity for orbital ordering arises from a splitting of the Mn dp levels by interaction with the 3d levels, which are associated with the Jahn-Teller distortion. Enhanced scattering from charge ordering originates from the small difference in the K-absorption energies associated with Mn3+ and Mn4+ sites, leading to anomalous scattering at the difference reflection. We used these techniques to investigate the interplay of charge and orbital ordering in PrFe2, Co3O4 with r = 0.4 and r = 0.8, and detected that below a common transition temperature of TC = 345 K the intensities of charge and orbital order show the same temperature dependence, with a considerable increase in intensity below the Neel temperature, indicating a coupling of the orbital and the magnetic degrees of freedom. It is further revealed that, in contrast to the charge order, the orbital order never achieves long range order, and an orbital domain state is formed. At temperatures above the transition we observe fluctuation loss of both charge and orbital order. Interestingly, the correlation length of the orbital order fluctuations decreases significantly faster with increasing temperature than the correlation length of the charge order fluctuations. This behavior suggests that the charge ordering drives the orbital ordering in these systems. This picture is confirmed by measurements where the phase transition is driven by the application of an external magnetic field. Y. Mukuoki et al. Phys. Rev. Lett. 80, 1382 (1998).

11:00 AM R11.2
BAND STRUCTURE OF Ni(100) VERSUS PERMALLOY(100).
F.1 Franco, T. Van Buuren, C. Bostedt, L. Terenziello, Lawrence Livermore National Laboratory, Livermore, CA; F.J. Hampel, Department of Physics, University of Wisconsin Madison, Madison, WI.

The magnetic characteristics of permalloy (Ni80Fe20) make this a material widely used in data storage technology. Sensors for hard disk reading heads have been using micromagnetic magnetoresistance (AMR) of permalloy or giant magnetoresistance (GMR) of permalloy/Cu/Cu thin films. It also has an unusually high density of minority spins [1]. Yet, only a few electronic structure studies have been published for permalloy, and many questions related to the unusual spin scattering remain open, e.g., the nature of the scattering states introduced by the Fe impurity. We have mapped the valence band of clean Ni(100) and epitaxial permalloy(100) by employing an imaging photoemission spectrometer coupled to an undulator-synchrotron-radiation beamline. Using the appropriate photon energies we are able to probe the high symmetry points in k-space at Γ(400) and X(300) and to compare the momentum distributions between Ni and permalloy. They differ, both in the 3d band and at the Fermi level. These differences will be discussed in the context of the electronic and magnetic properties, particularly regarding minority spin scattering states. [1] D.Y. Petrovykh, et al., Appl. Phys. Lett. 73, 3459 (1998). N. Pronko is support by the Spanish CICYT project CT96-0838. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

11:15 AM R11.3
HIGH ENERGY ANGLE RESOLVED PHOTOEMISSION STUDIES OF THE TEMPERATURE DEPENDENT ELECTRONIC STRUCTURE OF THERMOELECTRIC MATERIALS.
D.N. McKay, D. Zhang, Y. Kranov, B. Kempton, University of Idaho, Dept. of Physics, Moscow, ID; T.M. Pratt, R.T. Lissette, Clemson University, Dept. of Physics, Clemson, SC; C.G. Olson, Ames Laboratory, Ames, IA

ZeTe5 and HfTe5 are 2D layered systems where the layers interact via van der Waals like bonds. Both samples have two states within 6.5 eV of the Fermi level which quickly disperse downward from the Fermi level when moving away from the zone center. Low temperature spectra (20 K) were compared with spectra acquired at temperatures which corresponded to the peak in the electronic specific heat capacities of ZeTe5 and HfTe5, 170 K and 80 K, respectively. At the ZeTe5 transition temperature, the two states near the Fermi level shift closer together as they disperse toward the Fermi level. Similar shifts of the corresponding bands of HfTe5 at elevated temperatures were less obvious. We attribute this in part to the extremely small size of the Fermi surface of HfTe5 (0.150 Å-2) which makes it difficult to observe the photomission. These results suggest that the magnitudes of the effects observed for ZeTe5 may scale with Fermi surface size, or transition temperature, or a combination of both. The effects of doping on the properties of ZeTe5 and HfTe5 will also be addressed.

SESSION R12: X-RAY ABSORPTION SPECTROSCOPY OF MAGNETIC MATERIALS AND NANOARTICLES - II

Chair: Mark R. Antonio
Thursday afternoon, December 2, 1999
Suffolk (M)

1:30 PM R12.1
PHASE TRANSITION IN MnF2 - CaF2 SUPERLATTICES AND DOUBLE HETEROSTRUCTURES EPITAXIALLY GROWN ON Si(111).
Hosoko Oshichi, Masaaki Tsuchida, Yoshihiko Takeda, Dept. of Materials Science and Engineering, Graduate School of Engineering, Nagaoka Univ., Nagaoka, Japan; Alexander G. Banschick, Nikolai S. Sokolov, Nikolai L. Yakhovenko, Joffe Physico-Technical Inst., Russian Academy of Sciences, St. Petersburg, RUSSIA

Attractive optical and magnetic properties of rutile type structure MnF2 bulk crystals are well known. Antiferromagnetic ordering observed in these crystals below 67K and its manifestation in absorption and luminescence spectra have been studied in great details. Only few work was done, however, on epitaxial MnF2 layers, which are attractive for basic studies and have important potential applications. Epitaxial MnF2 has a possibility to form a cubic structure when grown on cubic CaF2. In this work, MnF2-CaF2 superlattices (SLs) and double heterostructures (DHSs) on Si(111) were investigated by fluorescence EXAFS using synchrotron radiation in order to find the coherency of the cubic structure influenced by fluoride CaF2 layers. The MnF2-CaF2 SLs and DHSs were grown by MBE on Si(111) with CaF2 buffer layer. The MnF2-CaF2 SLs consist of 15 periods. All the samples were capped by CaF2 layer. RXHEE measurements during the growth showed that the first 3ML of MnF2 on Si substrate grow coherently keeping cubic crystal structure. From the EXAFS analysis it was found that there are two types of Mn-F bond, i.e., the shorter one (2.12±0.03Å) and the longer one (2.28±0.03Å) in each sample that has different content ratio. The shorter Mn-F bond length was close to the average of the Mn-F bond lengths in rutile type MnF2. The longer Mn-F bond length was close to the Mn-F bond length [2.28Å] in fluorite type MnF2. The EXAFS analysis also revealed that in thin MnF2 layers (<3ML) the fluoride structure which does not exist at normal condition prevailed over the rutile structure, and the content ratio of the fluoride MnF2 strongly depended on the thickness of the MnF2 layer. Therefore, thin MnF2 layers coherently grow in fluoride structure on CaF2 and changed to
the rutile structure with the increase of MnF₂ layer thickness. The phase transition dependences of ESR line shapes and CI properties will be reported at the meeting.

1:45 PM R12.2
XANES ANALYSIS OF bcc/fcc-TWO-PHASE BINARY ALLOYS
Paul J. Schilling, Univ. of New Orleans, Dept. of Mechanical Engineering, New Orleans, LA; Roland C. Tittsworth, Louisiana State Univ., Center for Advanced Microstructures and Devices, Baton Rouge, LA; Evan Ma, Jinghao He, Johns Hopkins Univ., Dept. of Materials Science and Engineering, Baltimore, MD.

A critical factor in the characterization of two-phase binary alloy systems is the determination of the phase fractions and compositions of the two coexisting solid solutions for any given overall composition of the two-phase mixture. In some systems, for example nanocrystalline alloys formed by high-energy ball-milling, these parameters are difficult to attain by traditional techniques like X-ray diffraction. A new technique has been developed to obtain these quantities indirectly from X-ray absorption near edge structure (XANES) data collected at the two relevant absorption edges. The technique has been tested using Fe-Ni fcc and bcc standards and the results indicate that the method is accurate to within 5%. This method has been applied to two-phase (fcc and bcc) binary alloys formed by ball-milling. In mechanically alloyed Cu₆₆₋₆_Mn₃₄ (x = 50-80), the XANES analysis indicates that throughout this region the two coexisting phases have almost identical composition, consistent with that of the overall mixture. This represents a novel two-phase coexistence representing a system of overlap in solubility rather than the normal miscibility gap.

2:00 PM R12.3
EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDIES OF DOPED La₂Mg₁₋ₓMnₓO₃: THE RISE OF DISORDER IN COLOSSAL MAGNETORESISTANCE Y. G. Harris, Naval Research Laboratory, Washington, DC; J. O. Cross, Argonne National Laboratory, Argonne, IL; V. M. Browning, R. M. Stroud, and J. M. Byers, Naval Research Laboratory, Washington, DC.

The change in resistance in doped La₂MnO₄ in the presence of an applied magnetic field can exceed 1,000,000%. This unusually large magnetoresistance (a.k.a. colossal magnetoresistance or CMR) corresponds to a transition from paramagnetic insulator (PI) to a ferromagnetic metal (FM). A fundamental aspect of this transition is its extreme sensitivity to external perturbations, such as applied magnetic fields, strains or small changes in defect concentrations. In order to explore the role of disorder in the CMR of these materials we have employed ion irradiation to systematically damage the lattice of La₂₋₆₋ₓMnₓO₃ thin films. Extended x-ray absorption fine structure (EXAFS) analysis of the damaged films is performed using PEPF simulations, computed evolution, and the ratio method. We find that low radiation doses, expected to result in a small amount of damage, in fact leads to large local distortions around the Mn cations that lead to a dramatic change in the PEPF transition temperature from zero to full suppression, and an increase in the magnetoresistance from 600% to greater than 2,000,000%. It appears that the irradiation serves the role of a perturbation, allowing for significant alteration of the samples’ electronic properties. A variety of ion irradiation doses, and radiation effects on the role of processing, in particular the relative atomic disorder intrinsic to the processing technique, dictates the electronic behavior of the material. This explains the wide deviation in transport properties expected in the literature for samples having nearly identical stoichiometries but differing processing histories.

2:30 PM R12.4
USE OF FOCUSED SYNCHROTRON RADIATION FOR MICRO-XANES STUDIES OF LOCAL PHASES IN STEELS.
Philipp Dillmann, LP5 DRECAM CEA, CE Saclay, GIF Sur Yvette, FRANCE; Béatrice Regnau, Université de Technologie de Compiegne, Compagnie Générale Techer, Compiegne, Compagnie Codex, FRANCE.

The further development of new coal gasification fired power stations needs to study the behaviour of stainless steels in specific environments used to build the boiler. Particularly, their corrosion resistance must be evaluated at high temperature (about 400°C) when they are exposed to a complex atmosphere [H₂O, H₂, CO, CO₂] containing corrosion athermic gases. The aim is to know the proportion of each gas in vacuum. It is extremely important to understand the influence of the vanadium that is known to be very corrosive under certain condition. Thus, it is very useful to probe the local environment of vanadium in oxide scales formed on these steels by means of synchrotron photoelectron sources. The results of new studies on small samples with dimensions going down to few µm. Meanwhile focusing optics like capillary, bended mirrors, Bragg Fresnel and refractive lenses has been improved and now take advantage of new X-ray sources. Thus, we managed micro XANES experiments with the ESHF synchrotron beam, around the K edge of vanadium to study several stainless steels samples exposed to the specific environments mentioned above. We will show how, micro XANES studies combined with other ones more classical, will be very useful to understand the corrosion mechanisms in such environments.

3:15 PM R13.1
ELECTRONIC STRUCTURE OF Ge-NANOCLOUSTERS PROBED WITH SYNCHROTRON RADIATION C. Bostedt, University Hamburg, Hamburg, GERMANY and Lawrence Livermore National Laboratory, CA; T. Plc, N. Frances, and L.J. Terris, Lawrence Livermore National Laboratory, Livermore, CA; T. Moeller, Hesabyl at DESY, Hamburg, GERMANY.

Clusters and nanocrystals show a wide variety of novel electronic, magnetic and catalytic properties. Germanium clusters are of particular interest since, as recent publications suggest, they display a strong blue luminescence. However, it is not clear if this luminescence is due to surface species, oxide layers or quantum confinement. X-ray absorption spectroscopy (XAS) was performed on thin films of Germanium (Ge) clusters. The clusters were synthesized in situ by thermal vaporization of Ge in an Ar buffer gas and subsequently deposited on a hydrogen passivated Si substrate. The average diameter of the clusters could be varied between 2nm and 9nm. Characterization of the nanoclusters in size and shape was done by non-contact atomic force microscopy. XAS at the Ge L-edge was used to measure the shift of the conduction band of the Ge-clusters as a function of particle size. We find, that the conduction band of the clusters is blueshifted compared to bulk-Ge, in agreement with the quantum coherency theory. The blueshift ranges from 0.2eV to 0.4eV for clusters between 2nm and 2nm. No oxygen features are visible in XAS and XPS. Preliminary photomission data taken on clusters in the range from 2-9nm does not show any valence band shift, as these structures are too big for core-level excitation. Comparison of this work to previous work done on Si-clusters of the same size and prepared in the same manner show, that the conduction band shift in Si-clusters is much larger for clusters of the same size.

3:30 PM R13.2
CHARACTERIZATION OF CdS NANOPARTICLES GROWN IN GLASS. T. M Hayes and P. D. Persans, Rensselaer Polytechnic Institute, Dept of Physics, Troy, NY.

CdS nanoparticles well dispersed in a transparent medium can be grown by solid-phase precipitation from suitable precursors dissolved in borosilicate glass. The nanoparticle size distribution, composition, and structure must be controlled to produce composites usable in linear and nonlinear devices. This difficult task necessitates detailed characterization of the particles at all stages of nucleation, growth, and ripening. A crucial part of this is the use of x-ray absorption spectroscopy to study the band bending of Cd atoms at all stages. By combining this information with the results of optical spectroscopies, a remarkable amount can be deduced about particle size, composition, structure, and ultimately the thermodynamic properties of this complicated system. These results are presented.

3:45 PM R13.3

Capped nanoparticles have attracted great interest due to their versatility and tendency to form ordered arrangements. Here, we report a study of size-dependent structural parameters of thick-passivated gold nanoparticles (2-4 nm) such as inter-atomic
4:00 PM R14.3
REAL-TIME STUDY OF GRAIN GROWTH IN NANOCRYSTALLINE MATERIALS USING SYNCHROTRON RADIATION
C.E. Reil, University of the Saarland, Dept of Physics, Saarbrucken, GERMANY; H. Nater, University of the Saarland, Dept of Chemistry, Saarbrucken, GERMANY.

Improving the understanding of the kinetics of grain growth has been a primary goal of materials scientists since at least the 1940s. Experimental studies in this area have always been hampered by the laborious task of determining the grain size (D), which for conventional samples (D > 1 μm) involves optical microscopy of planar sections cut through a bulk specimen. Such preparation is destructive in nature, and the subsequent processing of optical micrographs necessary to obtain the average grain size and size distribution is usually quite time consuming, even with the use of advanced image analysis software. The recent development of techniques for nanocrystalline materials (D < 100 nm) has brought with it the possibility to study grain growth by x-ray diffraction, because the average size of the coherent scattering regions in such samples can be extracted from the broadening of Bragg peaks. In fact, by performing a Fourier analysis of the Bragg peak profiles, one can estimate not only the average grain size but also the size distribution. In measurements performed at the high-resolution powder diffractometry beamline BW16 at ESRF, we have followed the evolution of the grain size and size distribution in nanocrystalline samples held at elevated temperatures. The results have a direct bearing on recent theoretical models for grain growth, which predict a dependence on grain size. Kinetic models in the literature that may explain the unusual stability often observed in nanocrystalline materials. Real-time synchrotron studies of grain growth are well suited to probing such new aspects of an old phenomenon.

SESSION R14. X-RAY ABSORPTION SPECTROSCOPY
Chair: Debra R. Rabin and Paul J. Schilling
Friday Morning, December 3, 1999
Suffolk (M)

8:45 AM R14.1
THE STRUCTURE OF ACTINIDE IONS EXchanged INTO NATIVE AND MODIFIED ZEOLITES AND CLAYS.
Stephen R. Wasserman, Advanced Photon Source, Argonne National Laboratory, Argonne, IL; M. Soderholm, Daniel M. Giniquita, Chemistry Division, Argonne National Laboratory, Argonne, IL.

X-ray absorption spectroscopy, both XANES and EXAFS, has been used to investigate the structure and valence of thorium and uranium cations exchanged into microporous aluminosilicate minerals. The minerals used in this study consist of smectite clays and zeolites. XAS is used to examine the fate of the exchanged cations after modification of the mineral structure and/or exposure to hydrothermal conditions. These treatments serve as models for the forces that ultimately determine the chemical fate of actinide cations in the environment. The actinide speciation depends on the pore size of the aluminosilicate, which is fixed for the zeolite and variable for the smectite. The coordination and oxidation state of the actinide ions encapsulated within these structures are compared with those of the same ions in solution. Principal component analysis has been used to extract the conclusions reached from traditional methods for XAS analysis. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences-Chemical Sciences under contract W-31-109-ENG-38.

9:00 AM R14.2
SURFACE INTERACTIONS OF ACTINIDE IONS WITH GEOLOGIC MATERIALS STUDIED BY XAFS.
Patrick G. Allen, Eric R. Sylwester, Eric A. Hudson, Sandberg Institute, Lawrence Livermore National Laboratory, Livermore, CA.

We have investigated the interaction of the actinyl ion, UO_2^{2+}, with silica, alumina, and montmorillonite surfaces under ambient atmosphere and aqueous conditions using X-ray Absorption Fine Structure (XAFS) Spectroscopy. Characterization of mineral surface interactions with uranyl and other actinyl ions is complicated by the presence of multiple scattering paths which are signatures of the actinyl ion structure. These paths arise in the same region where weak interactions from third shell surface Si or Al atoms occur thereby complicating the structure determination. Details of the approaches to XAFS analysis in these systems will be discussed. In acid solution (pH ~ 3.5), the uranyl ion shows a strong interaction with the silica and alumina surfaces, and a redox weak association with the montmorillonite surface. The extent of direct surface interaction is determined by comparing structural distortions in the equatorial bonding environment of the uranyl ion relative to the framework of a free uranyl aquo complex. Based on this formalism, surface complexation on silica and alumina is through an inner-sphere mechanism with surface oxygen atoms binding directly to the uranyl ion region of the uranyl ion. In contrast, sorption on montmorillonite occurs on an outer-sphere mechanism in which the uranyl ion retains the simple aquo complex structure and binds to the surface via ion-exchange. In near-neutral solutions (pH ~ 6), sorption on all the materials is dominated by an inner-sphere mechanism. The formation of surface oligomeric species is also observed on silica and alumina. These findings are consistent with our results from a recent XAFS study which investigated uranyl interactions with vermiculite and hydrobiotite.

9:30 AM R14.3
THE INFLUENCE OF DESULFOVIBRIO DESULFURICANS ON NEPTUNIUM CHEMISTRY.
L. Soderholm, C.W. Williams, M.R. Aronson, Chemistry Division, Argonne National Laboratory, Argonne, IL; Monica Lee Tschirch and Michael Mardos, Benedictine University, Lisle, IL.

Desulfovibrio desulfuricans (DSV) is an anaerobic sulfur-reducing bacterium that is also known to change the oxidation state of iron during the course of its growth. Although iron reductors can sometimes be used for energy, sulfate is available as the electron acceptor in these experiments. The reduction of iron by DSV in these circumstances is possible because the Fe(III)/Fe(II) redox couple is accessible within the Eh/pH range of the growth medium. Neptunium (Np, atomic number 93) is a manmade, radioactive element that is of considerable concern because of its toxicity and mobility under environmentally-relevant conditions. Np is usually found in groundwater as the neptunyl (V) (\text{O}_2\text{Np}=\text{O}^+) moiety. Its reduction to tetraenium Np occurs at a standard potential similar to that of Fe(III). It is hypothesized that if the reduction potential is the primary factor in the behavior of iron in the presence of DSV, then Np(V) should behave in a similar manner. Experimental results used to determine the speciation of Np under biotic and abiotic conditions include x-ray diffraction, optical spectroscopy and x-ray absorption spectroscopy (XAS). Significant implications of Np(V) reduction by biotic processes will be outlined. This work is supported by U.S. DOE/Basic Energy Sciences, Chemical Sciences, and has benefited from the Actinide Facility at Argonne National Laboratory, all under contract W-31-109-ENG-38.

10:15 AM R14.4
X-RAY ABSORPTION STUDY OF ANTIWEAR FILMS GENERATED FROM ZDDP AND BORATE ADDITIVES.
K. Verlot, M. Kastar, J. M. Martin, B. Vacher, G. M. Bancroft, G. DeSimone, E. J. Yamaguchi, P. R. Ryman.

In 'limit lubrication', the protection against wear is due to the formation of tribochemical films on the surfaces in contact. These films are generated from the decomposition of lubricant additives. In engine oils for example, zinc dialkyldithiophosphate (ZDDPs) have been widely used as antioxidant and antiwear additive since the 40s. The demand for reduction of phosphorus/sulphur content in engine oils has forced the oil suppliers to develop new additives. Thus ZDDP content of oil should be replaced partially or totally by other additives. Organic borates are good candidates to replace ZDDP. X-ray absorption spectroscopy using the synchrotron radiation is used to characterize the local environment and in particular the hybridization of the boron atoms. The understanding of surface processes such as friction and wear is indeed of great interest as far as lubrication is concerned. This is not only to optimise the wear and friction but also to reduce pollution and energy consumption. In a first set of experiments, films such as engines or material shaping. Synchrotron radiation has revealed to be a powerful technique to probe both the surface and the bulk of tribochemical films. In this study, XANES spectroscopy was used to determine the chemistry of films created by three different borate additives, with and without ZDDP. The chemical structure of the additives has a great influence on the anti-wear efficiency and.
therefore on the chemistry of the tribrochemical films. Chemical imaging using the MUPHISTO microscopy beamline was performed to determine the distribution of different species present under applied rubbing. This will help to understand the mechanisms of formation of the tribrochemical films and the interactions between boric acid additives and ZDDP. 

10:30 AM R14.5
EXTRA-CELLULAR IRON-SULFUR PRECIPITATES FROM GROWTH OF DESULFOBACILLUS DESULFURICANS
Mark R. East, Chemistry Division, National Laboratory, Argonne, IL, Monica Tischler, Paul Wachtel, Benedictine University, Lisle, IL.
Sulfate reducing bacteria in subsurface oil reservoirs can cause petroleum production problems, especially in seawater flooding operations. Sulfate reducers are potent generators of hydrogen sulfide gas, H2S. Ulftrafine precipitates that form as a result of abiotic chemical reactions with H2S and iron can result in bacteria-related byproducts of microbial activity that foul operations. Oil recovery is negatively impacted when the precipitates clog the pores in the formation and reduce reservoir permeability. The resulting effects may lead to the premature decline in production. We have examined extracellular iron-bearing precipitates resulting from the growth of Desulfohacillus desulfuricans in a basal medium with lactate as the carbon source and ferrous sulfate. The precipitates formed as a result of bacterial growth were characterized by XAFS (X-ray absorption fine structure) and Mössbauer-effect spectroscopy. Comparisons with chemically synthesized precipitates and oilfield production solids from the Alaska North Slope were made. Our results and their implications to the geochemical habits of sulfate reducers in subsurface oil reservoirs will be discussed. This work was supported by the U.S. D.O.E. Office of Computational and Technology Research-Advanced Energy Projects, under contract W-31-109-ENG-38.

10:45 AM R14.6
CORROSION STUDIES USING X-RAY ABSORPTION TECHNIQUES: Hugh S. Isasi, Department of Applied Science, Brookhaven National Laboratory, Upton, NY.
X-ray absorption and fluorescence techniques employing synchrotron light have been employed to study corrosion. In situ observations of the chemical form and relative concentrations of elements have been determined using x-ray absorption near edge structure (XANES) under electrochemical control. For example chromium in its highly soluble 6-valent state is incorporated in passive films on iron and aluminum-chromium alloys and could be reduced electrochemically. The 6-valent state was stable on AI in air but was reduced on iron exposing the iron alloy. Critical concentrations of chromium in iron-chromium oxides have been identified. In situ x-ray fluorescence measurements, in conjunction with energy-dispersive analysis, have been used to identify iron, chromium, and nickel concentrations in solution and in salt layers. Their solubility and relative dissolution rates in pits have been determined. This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC03-76SF00098.

11:00 AM ★R14.7
IN SITU XAFS CHARACTERIZATION OF INTERMETALLIC AND METAL OXIDE INSERTION ELECTRODES FOR LITHIUM ION BATTERIES: A. Jereb, Krogstad, Chojnacki, Johnson, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.
Modern synchrotron x-ray sources have opened up new possibilities for in situ material characterization for processes that take from minutes to hours to complete. Time-resolved spectroscopy measurements in the past have been limited to specialized hardware. However, in third generation x-ray sources, general purpose spectroscopy stations are capable of time resolved measurements on the order of 1-10 minutes, ideal for studying processes that take hours to complete. Typical charge/discharge times for a battery are several hours, allowing many high-quality spectra to be collected during a cycle. A thin battery cell sealed in a plastic pouch has been used to make rapid measurements of x-ray absorption spectra at the Materials Research Collaborative Access Team (MRCAT) insertion device beamline at the Advanced Photon Source (APS). We report results on the structure of the hydrides Li4CoO2, Co3O4, and Li4MnO2, while cycling the cell over the range of 3.0 - 4.1 volts (x = 0.24 - 0.78). The x-ray absorption fine-structure spectroscopy (XAFS) data show a trend in the next-nearest-neighbor metal-metal bond lengths that suggest the Co atoms oxidize, and then at a point before the end of the charge cycle oxidize no further. Similarly, during the discharge portion of the cycle, the Co atoms are not reduced until the discharge cycle has progressed for some time. Time-resolved XAFS data will also be presented on a Cu2Sn2 intermetallic insertion electrode.

11:30 AM R14.8
EXAFS-DERIVED AMORPHOUS STRUCTURES IN RUTENIUM OXIDE IMPLICATIONS FOR CHARGE STORAGE MATERIALS: Karen E. Sevick, Patrick L. Hughes, Debra R. Robin, Surface Chemistry, Naval Research Laboratory, Washington, District of Columbia, United Kingdom.
Hydrous ruthenium oxide (RuO2-xH2O or RuO2-Hx) is a mixed electron/proton conductor with a specific capacitance as high as 900 F/g, making it a candidate material for energy storage. The structure-property correlation for RuO2-xH2O materials is not well understood due to their amorphous nature and compositional variability [i.e., the amount of structural water and the ratio of Ru(III) to Ru(IV)]. Extended x-ray fine structure (EXAFS) analyses show large differences in the short-range structures of the series as the water content (x) in the ruthenium structure increases from 0 to 2.3. Amorphous RuO2 has the rutile structure comprising chains of RuO6 octahedra linked in three dimensions, while the structure of RuO2.3H2O is rutile-like at the RuO2 core, but less connected and progressively disordered beyond the RuO2 core. The structure of RuO2.3H2O is composed of chains of disordered RuO6 octahedra that exhibit no chain-to-chain linking or three-dimensional order. Although the local structures of RuO2.3H2O and RuO2.3H2O markedly differ, the amount of electron/proton charge that they store is large and essentially equivalent. That is: non-unique local structures can express the same macroscopic property (charge storage) by balancing the competing electron/proton transport requirements necessary for charge storage. Coupling synchrotron characterization with synthetic techniques (such as preparation of hydrous ruthenium oxide as a nanoscale mesoporous material) and physical-chemical analyses permits interpretation of charge storage mechanisms in the technological material.

11:45 AM R14.9
SYNCHRONTRON-BASED STUDIES OF TRANSITION METAL INCORPORATION INTO SILICA-BASED SOL- GEL MATERIALS: Gwendolyn Mountjoy, Dave M. Pickup, Mark A. Holland, Robert J. Newport, Univ of Kent & Canterbury, School of Physical Sciences, Canterbury, UNITED KINGDOM; Graham W. Waladge, Mark E. Smith, Univ of Warwick, Dept of Physics, Coventry, UNITED KINGDOM.
The sol-gel preparation method provides a convenient route for the preparation of novel mixed-oxide materials. One such group of materials are silica-based xerogels incorporating TiO2 and ZrO2, with metal oxide contents from 5 to 40 mol%. These materials have potentially useful optical and catalytic properties. Their structures are also interesting because Ti and Zr are not compatible elements in an SiO2 network, and ordered binary compounds do not form under ambient conditions. Synchrotron-based techniques have made a key contribution to our multi-technique study of how TiO2 and ZrO2 groups are accommodated by the SiO2 network. EXAFS and XANES at the metal K-edge are elemental specific, and ideally suited to reveal the local environment of the metal atoms. In addition, SAXS is sensitive to the large scale distribution of metal atoms. Together these techniques provide a detailed picture of homogeneous mixing of metal atoms with the SiO2 network at low concentrations, and phase separation of metal oxide at high concentrations. Although TiO2 and ZrO2 xerogels show similar trends, there are important differences reflecting the different atomic properties of Ti and Zr.