

# SYMPOSIUM R

## Applications of Synchrotron Radiation Techniques to Materials Science

November 29 – December 3, 1999

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\* Invited paper

**2:00 PM R1.1**

**CHARGE TRANSFER AND LOCAL STRUCTURE IN THERMOELECTRIC GERMANIUM CLATHRATES.**

Anders 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 Furenliid, Univ of Arizona, Dept of Radiology, Tucson, AZ; George Nolas, Marlow Industries Inc, Dallas, TX; Dan Bryan, Susan Lattturner, 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 with rattling guest atoms of groups I or II. We have performed x-ray absorption studies (XANES and EXAFS) on a series of germanium based clathrates to quantify the charge transfer between the host and the guest atoms present, 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  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate Sr has 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 clathrate are close to those of the germanium and gallium metals, and ca. 5 eV 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 Buuren, Lawrence Livermore National Laboratory, Livermore, CA; G. Hart, University of California at Davis, Davis CA; C. Bostedt, N. Franco, J.E. Klepeis, L. J. Terminello, Lawrence Livermore National Laboratory, Livermore, CA; J. Terry, Los Alamos National Laboratory, Los Alamos, NM; J.R. Lince, Mechanics and Materials Technology Center, The Aerospace Corporation, El Segundo, CA.

All  $\text{MoS}_2$  (0002) single crystals investigated in this study were in the form of the natural mineral molybdenite, obtained from Ward's Natural Science establishment. A clean well-ordered surface of  $\text{MoS}_2$  (0002) was obtained by cleaving the top layers immediately before transfer into the UHV system followed by short anneal at 600C. The valence electronic structure of single crystal  $\text{MoS}_2$  was measured by synchrotron based, angle resolved photoemission using an imaging photoelectron spectrometer at beamline 8.0 of the Advanced Light Source. Photoelectron angular distribution images at a fixed kinetic energy were collected for a variety of photon energies. These images represent constant-energy contours in the  $\text{MoS}_2$  band structure. A set of such images can be assembled into a complete band structure of  $\text{MoS}_2$ . The constant energy contours are compared with band maps calculated within the local density approximation (LDA). We observe the valence band maximum (VBM) to be at the Gamma point with the appearance of features at the K-point 0.6 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 S atoms relax 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, in 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 the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD, N. Franco by the Spanish education and culture office.

**2:30 PM \*R1.3**

**X-RAY EXCITATION OF DX CENTERS IN  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .**

Yeong-Ah Soh, G. Aeppli, NEC Research Institute, Princeton, NJ; E.D. Isaacs, Lucent Technologies, Murray Hill, NJ; A. Frenkel, Brookhaven National Laboratory, Upton, NY; Frank M. Zimmermann, Rutgers University, Dept. of Physics and Laboratory for Surface Modification, Piscataway, NJ.

Si dopants in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  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-time 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 photoconductivity closely follows the simultaneously detected X-ray fluorescence, indicating that 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 K-edges, implying a non-local DX center excitation mechanism. We verified that this non-locality extends over macroscopic length scales by monitoring the photoconductance of a macroscopic sample excited by an X-ray microbeam.

**3:30 PM R1.4**

**DETERMINATION OF SURFACE ATOM POSITIONS WITH PHOTOELECTRON HOLOGRAPHIC IMAGING.**

G.J. Lapeyre, H. Wu, S.H. Xu, Y. Yang, H. Cruguel, M. Keeffe, Montana State Univ, Physics Dept, Bozeman, MT.

Angle-resolved core-level photoemission from an atom of interest contains diffraction 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 optional experimental conditions obtained from simulations will be presented. A theoretical basis for the rules will be given. Sites for a number of adsorbates have been measured for Si and GaN surfaces at the Wisconsin Synchrotron Radiation Center and the Advanced Light Source in Berkeley. Examples will be selected to show the power of the method. Research supported by ONR DEPSCoR and NSF. [1]. Huasheng Wu, G.J. Lapeyre, Phys. Rev. B 51, 14549 (1995)

**3:45 PM R1.5**

Abstract Withdrawn.

**4:00 PM R1.6**

**MAXIMUM ENTROPY METHOD CHARGE DENSITY DISTRIBUTIONS OF NOVEL THERMOELECTRIC CLATHRATES.**

Bo B. Iversen, Dept. of Chemistry, University of Aarhus, Aarhus, DENMARK; Anders E.C. Palmqvist, Dept. Applied Surface Chemistry, Chalmers University of Technology, Göteborg, SWEDEN; Dan Bryan, Susan Lattturner, Galen Stucky, Nick Blake, Horia Metiu, Dept. of Chemistry, University of California, Santa Barbara, CA; George S. Nolas, Marlow Industries Inc, Dallas, TX; Dave Cox, NSLS, Brookhaven National Laboratory, Upton, NY.

Recently materials with promising thermoelectric properties were discovered among the clathrates. Transport data has indicated that these materials have some of essential characteristics of a good thermoelectric, namely a low thermal conductivity and a high electronic conductivity. Based on powder and single crystal synchrotron X-ray diffraction data we have determined the charge density distributions in a number of closely related semiconducting clathrate materials ( $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ ,  $\text{Ca}_x\text{Sr}_{8-x}\text{Ga}_{16}\text{Ge}_{30}$ ,  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ ,  $\text{Ca}_x\text{Ba}_{8-x}\text{Ga}_{16}\text{Ge}_{30}$ ) using the Maximum Entropy Method. Analysis of charge distributions can provide answers to two important questions related to thermoelectric properties, 1) Are the guest atoms rattling?, 2) What is the nature of the chemical interactions between the guest atoms and the framework? Guest atom rattling can significantly lower the thermal conductivity through phonon scattering processes, whereas the guest-host interactions affect the electronic conduction. Results for the above mentioned structures will be presented.

**4:15 PM R1.7**

**INVESTIGATION OF INHOMOGENEOUS STRAIN RELAXATION IN DRY ETCHED SiGe/Si QUANTUM WIRES USING X-RAY GRAZING-INCIDENCE DIFFRACTION.**

Y. Zhuang, J. Stangl, T. Roch, G. Bauer, S. Zerlauth, F. Schäffler, Institut für Halbleiterphysik, Johannes Kepler Universität Linz, Linz, AUSTRIA; U. Pietsch, N. Darowski, Institut für Physik, Universität Potsdam, Potsdam, GERMANY; V. Holy, Laboratory of Thin Films and Nanostructures, Masaryk University, Brno, CZECH REPUBLIC.

Surface sensitive x-ray grazing-incidence diffraction (GID) was employed to investigate the elastic strain relaxation in lateral periodically arranged SiGe/Si quantum wires which were fabricated from a ten period pseudomorphic MBE-grown  $\text{Si}_{0.82}\text{Ge}_{0.18}$ /Si superlattice on (001) Si wafer. The wires pattern aligned along [110] direction with a period of about 460 nm were defined by holographic lithography and generated by reactive ion etching. Four samples were fabricated with different etching depth varying from 90 nm to 300 nm

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. GID measurements performed 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  $q[1\bar{1}0]$ ) scans were performed at different incidence angles, i.e. different penetration depth. At  $q_x$  positions of the respective grating peaks truncation rod intensities were recorded. Using the data from FEM and taking into account a modified effective refraction index for the wires pattern the curve simulation based on a DWBA approach of GID is in good agreement with 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, 1999  
Suffolk (M)

9:00 AM R2.1

ANOMALOUS ULTRA-SMALL-ANGLE X-RAY SCATTERING BY  
EVOLVING MICROSTRUCTURES DURING TENSILE CREEP.  
P.R. Jemian, Univ. of Illinois at Urbana-Champaign, Urbana, IL;  
G.G. Long, F. Lofaj 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 significantly 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 a 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 with 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  $L_{III}$  edges of the rare-earth oxide secondary phases. Both (cavity 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; Pete R. Jemian, University of Illinois at  
Urbana-Champaign, Materials Research Lab, Urbana, IL; G.R.  
Odette, D. Klingensmith, D. Gragg, University of California at Santa  
Barbara, Department of Mechanical and Environmental Engineering,  
Santa Barbara, CA; S. Seifert, Argonne National Laboratory,  
Chemistry Division, Argonne, IL.

As nuclear power plants age, understanding radiation-induced materials degradation is essential for safe plant performance 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 embrittled microstructure present in irradiated reactor 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 such, provide important input into mechanistic hardening models used to interpret embrittlement. In this work ASAXS experiments have been performed at the Advance Photon Source on a model Fe-0.9 wt.% Cu-1.0 wt.% Mn RPV alloy. The material was characterized in the

following forms: as-prepared (i.e. untreated), thermally annealed (450°C, 24 hours), and electron irradiated (10 MeV electrons, 300°C). The evolution of the microstructure with radiation dose was examined for damage levels  $\leq 10^{-3}$  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 14Å and 8Å 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 presence of copper-rich precipitates. This work was supported in part by the US Department of Energy, BES-Materials Sciences, under contract No. W-31-109-ENG-38.

9:30 AM R2.3

IN-SITU STUDIES OF THE PROCESSING OF SOL-GEL  
PRODUCED AMORPHOUS MATERIALS USING CURVED IMAGE  
PLATE XRD, XANES AND SAXS. Dave M. Pickup, Gavin  
Mountjoy, 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, Daresbury 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 SAXS parallel channel, experimental methods including: i. time-resolved small angle scattering, using a quadrant detector, to follow the initial stages of aggregation 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 plate detector in diffraction, which allows the simultaneous collection of data across a wide range of scattering ( $2\theta = 0^\circ$  to  $120^\circ$  at  $\lambda = 0.7 \text{ \AA}$ ) at high count rate, to study heat treatments. iii. X-ray Absorption Near Edge Structure to explore, as a function of heat treatment, the reversible/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:titania binary materials, studied from the polymerisation stage, through xerogel to high density calcined solid. Titania contents 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  $^{29}\text{Si}$  and  $^{17}\text{O}$  mas-NMR and other spectroscopic data. The project provides a clear example of the efficacy of modern synchrotron methods in condensed matter science when used 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

PROBING THE ELECTRICAL DOUBLE-LAYER STRUCTURE AT  
THE RUTILE-WATER INTERFACE WITH X-RAY STANDING  
WAVES. P. Fenter<sup>1</sup>, L. Cheng<sup>2</sup>, S. Rihs<sup>1</sup>, M. Machesky<sup>3</sup>, P.  
Geissbühler<sup>4</sup>, M.J. Bedzyk<sup>1,2</sup> and N.C. Sturchio<sup>1</sup>, <sup>1</sup>Argonne National  
Laboratory, Argonne IL; <sup>2</sup>Northwestern University, Evanston IL;  
<sup>3</sup>Illinois State Water Survey, Champaign IL; <sup>4</sup>University of  
Washington, Seattle WA.

Knowledge of the distribution of ions at the solid-liquid interface is fundamentally important for understanding its properties. 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(+2) and Rb(+1) ions with the rutile TiO<sub>2</sub> (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 stable over a broad 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 in the condensed ion layer. 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 the study of molecular ordering at liquid-liquid interfaces. This includes studies of the following systems: (a) structure and phase transitions in a soluble fluorinated monolayer at the water-hexane interface; (b) structure at pure water-alkane interfaces; (c) structure of phospholipid monolayers at the water-heptane 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 SURFACTANT SPECIFIC PROTEIN SP-B INTO LIPID MONOLAYERS AT THE AIR-FLUID INTERFACE. Ka Yee C. Lee, The University of Chicago, Dept of Chemistry, Chicago, IL; Jaroslaw Majewski, Greg S. Smith, Los Alamos National Laboratory, Manuel Lujan Jr. Neutron Scattering Center, Los Alamos, NM; Tonya Kuhl, Joseph A. Zasadzinski, UCSB, Dept of Chemical Engineering, Santa Barbara, CA; Paul B. Howes, Kristian Kjaer, Risoe National Laboratory, Dept of Solid State Physics, Roskilde, DENMARK; Michael M. Lipp, MIT, Dept of Chemical Engineering, Cambridge, MA; Alan J. Waring, MLK Jr./Drew Medical Center and UCLA, Los Angeles, CA.

We report the first x-ray scattering measurements to determine the effects of SP-B1-25, the N-terminus peptide of lung surfactant specific protein SP-B, on the structure of palmitic acid (PA) monolayers. In-plane diffraction shows that the peptide fluidizes a portion of 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 shows that the peptide is oriented in the lipid monolayer at an angle of  $\sim 34^\circ$  relative to the interface, with one end protruding past the hydrophilic region into the fluid subphase, 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 d-spacings of the ordered collapse phase seem to be independent of the peptide. The interplanar distances agree well with powder diffraction data on palmitic acid. 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.

Yufei Hu, L.J. Martinez-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 alignment of the films as a function of depth and temperature. Our results indicate the presence of both a chevron structure and a structure similar to the helical twist-grain-boundary (TGB) phase. Some films have a disordered interfacial layer. 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 Grants Nos. ECS-95-30933 and ECS-96-96069. 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)

#### 1:30 PM \*R4.1

##### REAL-TIME CHARACTERIZATION OF BIOGEOCHEMICAL

##### PROCESSES ON SURFACES OF GEOLOGIC MATERIALS BY SR-FTIR SPECTROMICROSCOPIC IMAGING.

Hoi-Ying N. Holman, Center for Environmental Biotechnology, and Department of Ecology; E.O. Lawrence Berkeley National Laboratory, Berkeley, CA.

The success of using intrinsic microorganisms to detoxify metal ions of high oxidation state and to degrade organic hydrocarbons has been hindered by the lack of fundamental understandings of their transformation and remobilization on surfaces of geologic materials. This is due to the previous lack of appropriate instrumentation that can overcome the heterogeneous nature of surfaces of geologic materials and at the same time can nondestructively evaluate the progressing microbe-driven biogeochemical processes at the chemical/microbe interface. To meet this technology gap, we are currently exploring the use of Synchrotron Radiation-based (SR) Fourier transform infrared (FTIR) spectromicroscopy in the mid-IR region as a microprobe to study the localization and progress of biogeochemical processes as they are occurring at the interfaces. To date, we have applied the SR-FTIR spectromicroscopy technique to study the biotransformation of metal ions of high oxidation state [e.g., chromate ( $\text{CrO}_4^{2-}$ ), dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ )] and to study the progress of biodegradation of organic hydrocarbons [e.g., toluene, pyrene] on mineral surfaces. In this presentation, band intensities and band intensity ratios for functional groups of these metal molecules and organic hydrocarbons will be discussed in the context of molecular components as they are perturbed by interactions with biomolecules which are inherent to biogeochemical systems. Time-resolved SR FTIR spectra and mapping of the spectral markers for the biogeochemical reactions at the interface will be presented and discussed. With this experimental effort, the usefulness of SR-FTIR spectromicroscopy as a promising tool to complement existing techniques for studying the fate of metal ions of high oxidation state and the progress of biodegradation of organic hydrocarbons on mineral surfaces occupied by microorganisms has been demonstrated.

#### 2:00 PM R4.2

##### SYNCHROTRON STUDIES OF THE CHEMISTRY OF $\text{SO}_2$ AND $\text{H}_2\text{S}$ ON MGO SURFACES. A.E. Freitag, J.Z. Laresse, Chemistry Department, Brookhaven National Laboratory, Upton, NY.

The release of sulfur oxides ( $\text{SO}_x$ ) during the burning of fuels constitutes a major environmental problem. Increased regulations affecting the control of environmental pollution require new, more efficient catalysts to be developed for the removal and destruction of  $\text{SO}_x$  compounds. It has been suggested that catalysts based on pure and metal promoted magnesium oxide can accomplish this goal. Limited microscopic information currently exists on how these compounds interact with sulfur oxides or how they operate at elevated temperatures (400-800K) and pressures (1- 2 atm). Using in-situ time-resolved x-ray diffraction, XANES near the sulfur K-edge, adsorption isotherms and TPD we have begun to address these issues. We will report on investigations of the behavior of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  with MgO.  $\text{SO}_2/\text{MgO}$  isotherms show a fifty percent decrease in  $\text{SO}_2$  adsorption on MgO powders previously exposed to monolayer quantities of  $\text{SO}_2$ , even after warming to room temperature and pumping on the pretreated powder. Subsequent TPD measurements indicated that the MgO must be heated to  $T > 350^\circ\text{C}$  to remove the adsorbed sulfur species. XANES measurements on pre-dosed samples clearly indicate that both  $\text{SO}_3$  and  $\text{SO}_4$  species are present at room temperature. XANES measurements were performed after several stepwise heating/pumping cycles of the  $\text{SO}_2$  treated samples. Reduction of both the  $\text{SO}_3$  and  $\text{SO}_4$  species occurs as the temperature is increased with no signals present at temperatures above about  $350^\circ\text{C}$ . Thin films ( $\geq 1$  mnl) of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  have also been studied on MgO in-situ using x-ray diffraction (XRD) while simultaneously performing an adsorption isotherm. We will discuss the microscopic structure and changes in the XRD as a function of temperature. This work was supported by the U.S. Dept. of Energy, Materials Science Division, under Contract No. DE-AC02-98CHI0886.

#### 2:15 PM \*R4.3

##### X-RAY SPECTRO-MICROSCOPY AND MICRO-SPECTROSCOPY IN THE 2100 eV TO 12000 eV REGION. Nicholas Moelders, Louisiana State Univ, CAMD, Baton Rouge, LA; Paul J. Schilling, Univ 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  $18.8 \mu\text{m} \times 7.0 \mu\text{m}$  ( $\sigma$ ), respectively. The beamline and end-station are designed and optimized to perform (i) spatially-resolved x-ray fluorescence spectroscopy (spectro-microscopy) using the broad intense spectrum of the white synchrotron radiation, and (ii) spatially-resolved x-ray absorption spectroscopy (micro-spectroscopy) in the energy region of

2100 eV to 12000 eV. These dual capabilities enable K-edge measurements and mapping, in non-vacuum conditions, of low-Z elements down to Cl, S, and P, that are of both environmental interest and technological importance. In this paper, an application of this novel synchrotron tool to elucidate the elemental distribution (microstructure) and chemical state (speciation) of Mn, Cl, S, and P-containing particulates emitted from automobile engines burning methylcyclopentadienyl manganese tricarbonyl- (MMT-) added fuel will be discussed in detail. Future opportunities of this microbeam technique in materials science and materials characterization will also be outlined.

#### 2:45 PM R4.4

DIAMOND IN-LINE MONITORS FOR DEMANDING SYNCHROTRON EXPERIMENTS. P. Bergonzo, D. Tromson, A. Brambilla, C. Mer, B. Guizard, F. Foulon, LETI (CEA - Technologies Avancées)/DEIN/SPE, 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 hundredths micrometers can be fabricated and assembled either as membranes or as 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 dependant X-ray spectroscopy. Highly transparent beam position monitors (BPM) were made that exhibit at 4 keV a position resolution better than 2  $\mu\text{m}$ . 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 potentialities for diamond towards the fabrication of synchrotron light characterisation tools.

### SESSION R5: SPECTROMICROSCOPY & 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, near-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 failure 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 nm. 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 to 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; Michael Dudley, Dept. of Materials Science, State University of New York at Stony Brook, Stony Brook, NY.

Synchrotron X-ray topography has been used to study dislocation behavior around notches in single crystals of ice during in-situ deformation at a constant strain-rate. During deformation at  $-8^{\circ}\text{C}$  a dislocation depleted zone (DDZ) formed above the notch while 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 effects of temperature on dislocation behavior around notches in ice under uniaxial tension was explored with dislocation activity around the notch at  $-8^{\circ}\text{C}$  observed to be much greater than the activity at  $-40^{\circ}\text{C}$  and  $-60^{\circ}\text{C}$ . Acknowledgements: Grant OPP-9526454 from the National Science Foundation and Grant DAA-H04-96-1-0041 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 Laor, NIST, Gaithersburg, & NRC, 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 crystals grown in space exceed those of terrestrial crystals; through diffraction imaging this superiority has been traced to specific differences in crystalline regularity. As a result of the knowledge gained from these observations, substantial enhancement 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 marked progress in the transport properties of 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 convection in microgravity appears to be far more influential 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 50%. 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 optimized and that they may ultimately surpass 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

Chairs: Susan M. Mini and Tony W.H. van Buuren  
Wednesday Morning, December 1, 1999  
Suffolk (M)

#### 9:00 AM R6.1

TIME RESOLVED STUDIES OF PHASE TRANSFORMATIONS USING HIGH TEMPERATURE POWDER DIFFRACTION. L. Margulies, M.J. Kramer, R.W. McCallum and A.I. Goldman, Ames Laboratory, ISU, Ames, IA; D. Haefner, APS, Argonne National Laboratory, Chicago, IL; S. Kycia, CHESS, Cornell University, Ithaca, NY.

Analyses of time resolved structural changes enable an understanding of the competing 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 ends, a high temperature furnace (up to  $1500^{\circ}\text{C}$ ) 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 image plate detector system has allowed powder patterns to be collected with a time resolution on the order of a few seconds. The kinetics of phase transformations are studied by performing Rietveld refinement on multiple spectra collected throughout the transformation process. Data collected on the orthorhombic to rhombohedral transition in  $\text{SrCO}_3$  and the tetragonal to cubic transition in the RhTi systems 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, Jonathan C. Hanson, Sanjay Chaturvedi, Brookhaven National Laboratory, Upton, NY; Joaquin L. Brito, Venezuelan Institute of Scientific Research, Caracas, VENEZUELA; Amitesh 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 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 dehydration of zeolites, the binding of substrates and 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 a 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 L- 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  $\text{ZrW}_2\text{O}_8$ . Cora Lind, Angus P. Wilkinson, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA; Michael T. Vaughan, Donald J. Weidner, Jihua 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 that seen in cubic  $\text{ZrW}_2\text{O}_8$  (transformation to an orthorhombic phase at 2.5 kbar) are thus undesirable, as the original expansion properties are lost. We have investigated the high pressure behavior of the NTE materials cubic  $\text{ZrMo}_2\text{O}_8$  and cubic  $\text{HfMo}_2\text{O}_8$  in a high pressure cell using synchrotron radiation for in situ observation. Experiments were carried out at pressures up to 30 kbar and 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 4-5 kbar, while no structural changes could be 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 the thermodynamically stable form of  $\text{ZrMo}_2\text{O}_8$  but had not been seen for  $\text{HfMo}_2\text{O}_8$  prior to this work

#### 10:15 AM R6.4

HIGH REAL-SPACE RESOLUTION STRUCTURE OF MATERIALS BY HIGH-ENERGY X-RAY DIFFRACTION. Th.

Proffen, V. Petkov, I-K. Jeong and S.J.L. Billinge, Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

Many materials of modern technological interest are not perfectly crystalline but contain intrinsic disorder. Quite often this disorder gives rise to interesting properties and it is important to be characterized. We have been acting developing the approach of obtaining high-resolution atomic pair distribution functions (PDFs) to study it. Using high energy X-ray diffraction we obtained very high real-space resolution PDFs and studied a number of materials science problems. Results of two recent experiments will be presented. The first one concerns a determination of the bond-length distribution and internal strain in In-Ga-As semiconductor alloys. The second - a determination of concentration and temperature dependence of Jahn-Teller distortions in colossal magnetoresistance La-Ca-Mn-O materials.

#### 10:30 AM \*R6.5

HIGH ENERGY SYNCHROTRON RADIATION DIFFRACTION EXPERIMENTS IN MATERIALS SCIENCE. Jochen R. Schneider. Deutsches Elektronen-Synchrotron DESY, Hamburg, GERMANY.

Modern synchrotron radiation facilities provide very intense X-ray beams with energies of the order 100 keV and even above. They provide a new probe for condensed matter research combining the high penetration power of thermal neutrons with extreme momentum space resolution of state of the art X-ray diffractometers. A short presentation of the 3 crystal diffractometers installed at a wiggler beamline at the storage ring DORIS and an undulator beamline at the storage ring PETRA operated at 12 GeV electron energy is followed by a discussion of the diffraction properties of Si-Ge gradient crystals, which are used as monochromator and analyzer crystals. As to applications emphasis is on accurate charge density measurements, structural phase transitions in perovskites and high  $T_c$  superconductors, and the determination of the local texture and internal strain inside bulky components.

#### 11:00 AM R6.6

A SYNCHROTRON RADIATION STUDY OF THE PHASE FRACTION, TEXTURE AND STRAIN EVOLUTION IN SUPERELASTIC NiTi. Raj Vaidyanathan, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA; Safak Yilmaz, David C. Dunand, Northwestern University, Department of Materials Science and Engineering, Evanston, IL.

The stress-induced transformation of nickel-rich NiTi from the cubic (B2) austenite phase to the monoclinic (B19') martensite phase can result in tensile strains as high as 8% under applied stress. On unloading, the martensite becomes unstable and transforms back to austenite, with a concomitant macroscopic strain recovery. Synchrotron X-ray spectra were obtained in transmission during various stages of this reversible, stress-induced, austenite-martensite phase transformation in wire samples of polycrystalline superelastic NiTi subjected to mechanical loading. The advantage of using synchrotron X-rays over a conventional X-ray source is that the measurements are taken over the bulk of the sample, of importance since the stress state at the surface of polycrystalline NiTi is expected to be different. Furthermore, the advantage over neutron diffraction is that X-ray measurements are about ten times faster than those conducted at existing neutron sources. Results of the phase volume fraction, texture and strain evolution are presented as a function of applied stress as the austenite gradually transforms to martensite with stress (and transforms back on unloading). The results are compared to similar results obtained from neutron diffraction measurements and the role of starting texture discussed.

#### 11:15 AM R6.7

SYNCHROTRON X-RAY DIFFRACTION STUDY OF ELASTIC PHASE STRAINS IN THE BULK OF EXTERNALLY LOADED Cu/Mo COMPOSITES. Alexander Wanner, Institut fuer Metallkunde, Universitaet Stuttgart, Stuttgart, GERMANY; David C. Dunand, Dept of Materials Science and Engineering, Northwestern University, Evanston, IL.

Classical techniques to measure elastic strains in the bulk of a crystalline solid are based on the diffraction of thermal neutrons. While these techniques have proven to be extremely powerful tools for many applications, the measurement times are long and/or the diffracting specimen volumes are large due to the low fluxes available at current neutron sources. The availability of high-energy photons from 3rd generation synchrotron research facilities offers alternative approaches to internal strain diffraction measurements which do not have these restrictions and are therefore a complementary tool to neutron diffraction. We have applied a synchrotron radiation transmission technique to study the internal load transfer and

micromechanical damage in two-phase Cu-Mo alloys during plastic deformation. Mechanically-loaded, 1.5 mm thick specimen irradiated with a monochromatic beam of 65 keV photons at 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 phase strains can be calculated) but also the ring graininess (which is related to the peak broadening). Based on this information, we characterized the deformation 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: MICRO-DIFFRACTION  
Chair: Uta Ruett  
Wednesday Afternoon, December 1, 1999  
Suffolk (M)

#### 1:30 PM R7.1

X-RAY MICRODIFFRACTION STUDY OF Cu INTERCONNECTS. X. Zhang, H. Solak, F. Cerrina, Electrical and Computer Engineering and Center of Nanotechnology, University of Wisconsin-Madison; B. Lai, Z. Cai, P. Ilinski, D. Legnini, W. Rodrigues, Advanced Photon Source, Argonne National Laboratory.

Copper has been chosen as the interconnect material to replace Aluminum-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 electrical 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  $5\mu\text{m}$  to  $0.25\mu\text{m}$ . The length of all lines was 1mm. An electron beam evaporation was used to deposit Cu(350nm) or Ti(20nm)/Cu(350nm) films on these wafers. SiN( $0.2\mu\text{m}$ ) and SiO( $0.4\mu\text{m}$ ) were deposited as passivation layer using plasma-enhanced chemical vapor deposition at  $350^\circ\text{C}$ . All samples were annealed at  $450^\circ\text{C}$  for 30 minutes in a  $\text{N}_2(90\%)/\text{H}_2(10\%)$  mixture.

The X-ray microdiffraction experiments were conducted at Argonne National Laboratory. The phase zone plate based micro-beam beamline 2-ID-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 experiment are sensitive only to the surface normal direction. The beam spot used in this experiment is about  $1\mu\text{m}$  in vertical direction and  $5\mu\text{m}$  in horizontal direction.

From our experiment, we found Titanium adhesion layer has a significant effect on Copper interconnect microstructures. Without Titanium adhesion layer, the as-deposited Cu shows no texture and has bigger grains. With Titanium adhesion layer, the as-deposited Cu interconnect has (111) texture and smaller grains. It also has a wide 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 more 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 anode pad has been found directly from Copper fluorescence. The X-ray microdiffraction around the void area shows significant strain variations. Our data shows that the strain becomes compressive around the hillock region, and becomes more tensile around void region. Diffraction from CuTi alloys was also detected around the void area.

#### 1:45 PM R7.2

NONDESTRUCTIVE DETERMINATION OF THE DEPTH OF DIFFERENT TEXTURE COMPONENTS IN POLYCRYSTALLINE SAMPLES. C.P. Patterson II, K.I. Ignatiev, A. Guvenilir, 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 (macrotexture) 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 materials 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

tracing the diffracted rays back to their physical origin. Polychromatic synchrotron x-radiation and absorption edge filters are used. Results from sections of Al-Li 2090 T8E41 plates are reported, and limitations of this ray tracing technique are discussed.

#### 2:00 PM \*R7.3

PLASTIC DEFORMATION, RECRYSTALLIZATION AND INTERNAL STRESSES STUDIED BY A NEW 3D X-RAY MICROSCOPE. D. Juul 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 only a small ( $\mu$ -sized) selected volume in the bulk of a sample. Thereby 3D characterizations at a microstructural relevant scale become a reality. In the first part of the presentation, the experimental set-up is described. In collaboration with ESRF staff 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. Very little quantitative information is presently available on these processes because of the lack of an adequate experimental technique.

- **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 polycrystal plasticity.

#### 2:30 PM R7.4

3-D MEASUREMENT OF DEFORMATION MICROSTRUCTURE IN Al(0.2%)Mg USING SUBMICRON RESOLUTION WHITE X-RAY MICROBEAMS. B.C. Larson, N. Tamura, J.-S. Chung, G.E. Ice, Oak Ridge National Laboratory, Oak Ridge, TN, H. Weiland, Alcoa Technical Center, Alcoa Center, PA, and W. L. Lowe, Howard University, Washington DC.

We have used submicron resolution white x-ray microbeams on the MHATT-CAT beamline at the Advanced Photon Source to investigate, in three-dimensions, the deformation microstructure in a 20% plane strain compressed Al(0.2%)Mg tri-crystal. K-B mirrors were used to focus the white beam of the MHATT-CAT undulator to a  $0.7 \times 0.7 \mu\text{m}^2$  beam, which was scanned over bi- and tri-crystal regions near the triple junction of the tri-crystal. White beam Laue photographs were collected using a CCD x-ray detector. Depth resolution along the x-ray microbeam of  $\sim 2$ -3 microns was achieved by triangulation back to the diffraction source point through the use of CCD pictures taken at a 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 orientations 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 microstructural evolution will be discussed.

\*Research sponsored by the U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. N. Tamura and J.-S. Chung are supported under the ORNL Postdoctoral Research Associates Program administered jointly by ORNL and ORISE. The x-ray measurements were performed on the MHATT-CAT beam line at the APS. The APS is supported by the DOE Office of Energy Research under contract W-31-109-ENG-38.

#### 2:45 PM R7.5

LOCAL STRAIN MEASUREMENT TECHNIQUES IN BULK MATERIALS. U. Lienert, S. Grigull, A. Kvick, R.V. Martins, ESRF, Grenoble, FRANCE; H.F. Poulsen, E.M. Lauridsen, S.F. Nielsen, Risoe Nat. Lab., Roskilde, DENMARK.

An experimental station dedicated to the local structural characterization of bulk materials has been set-up at the ESRF. High energy synchrotron radiation (40-90 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-focussing, broad band monochromators and position sensitive detection systems behind the sample. We are aiming for a 3-dimensional gauge volume of 5x5x50 micrometers whereas a resolution down to 1 micrometer can be achieved in 1 dimension. The technique is non-destructive and allows for in-situ investigations of thermo-mechanical processing. This presentation focusses on the measurement of the local strain/stress state. The development of a strain scanner with micrometer sized gauge volume is described by experimental case 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 sample, the transition from the single grain to powder 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 PM R8.1**

**APPLICATION OF SYNCHROTRON RADIATION TO IN VIVO MICRO-TOMOGRAPHY: THE OVX RAT MODEL OF OSTEOPOROSIS.** J.H. Kinney, University of California, San Francisco, CA; D.L. Haupt, 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 interconnecting 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 natural collimation 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 ovariectomized rats, 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 beyond 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 (RO1-AR 43052), and by the US DOE Basic Energy Sciences Division which supports SSRL.

**3:45 PM R8.2**

**ATTENUATION- AND PHASE-CONTRAST MICRO-TOMOGRAPHY USING SYNCHROTRON RADIATION FOR THE 3-DIM. INVESTIGATION OF SPECIMENS CONSISTING OF WEAKLY AND NORMALLY ABSORBING ELEMENTS.** Felix Beckmann, Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, GERMANY; Ulrich Bonse, 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 material science. Using attenuation 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 PM R8.3**

**X-RAY PHASE CONTRAST IMAGING STUDY OF ACTIVATED CARBON/CARBON COMPOSITE.** Kenji Kobayashi, Koichi Izumi, Hidekazu Kimura, Sigeru Kimura, Tomoaki Ohira, NEC Corporation, Fundamental Research Laboratories, Tsukuba, JAPAN; Takashi Saito, Yukari Kibi, Fundamental Material Research Laboratories, NEC Corporation, Kawasaki, JAPAN; Kengo Takai, Takashi Ibuki, Yasushi Kagoshima, Junji Matsui, Fac. of Science, Himeji Inst. of Tech., Aka, 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  $b$ ). 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-beamline 24XU in SPring-8. The x-rays emitted from the 8-figure undulator were monochromatized to  $\lambda = 0.83 \text{ \AA}$  by using the Si (111) double crystal monochromator. The typical beam size was  $1 \times 1 \text{ mm}^2$  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  $2 \text{ \mu m}$ . We applied this method to activated carbon/carbon composite which are used as electrodes of electric double-layer capacitors (EDLCs) so that it was possible to observe the phase contrast corresponding to the carbon particle with  $10 \text{ \mu m}$ .

**4:15 PM R8.4**

**SYNCHROTRON X-RAY SCATTERING STUDY OF THE OXIDATION OF AlN/SAPPHIRE(0001) FILMS.** Hyon Chol Kang, Seon Hee Seo, and Do Young Noh, Kwangju Institute of Science and Technology, Dept of Materials Science and Engineering, Kwangju, KOREA.

The structural transformation of AlN/Sapphire(0001) thin films into epitaxial AlON thin films during thermal oxidation was studied by in-situ synchrotron x-ray scattering measurements. The formation of AlON started as the AlN films are annealed to  $\sim 750^\circ\text{C}$ , and completed at  $950^\circ\text{C}$ . The film surface roughened gradually as AlON was formed. The AlON films have cubic spinel structure with the  $\langle 111 \rangle$  direction parallel to the substrate normal, sapphire  $\langle 0001 \rangle$  direction. The in-plane crystalline axis was rotated by  $30^\circ$ , resulting AlON  $\langle 1\bar{1}0 \rangle$ //sapphire  $\langle 10\bar{1}0 \rangle$  and AlON  $\langle 1\bar{2}1 \rangle$ //sapphire  $\langle 11\bar{2}0 \rangle$ . The lattice constant of AlON changed from  $7.992 \text{ \AA}$  to  $8.102 \text{ \AA}$  as the oxidation proceeds at  $950^\circ\text{C}$ , which is attributed to the change of oxygen content. The in-plane (surface normal) domain size of AlON films also increased from  $92 \text{ \AA}$  ( $85 \text{ \AA}$ ) to  $250 \text{ \AA}$  ( $280 \text{ \AA}$ ), respectively. This suggests that the nano-size AlON crystalline was initially formed, and the grain-growth progressed gradually.

**4:30 PM R8.5**

**STRUCTURE OF THE NEAR-SURFACE WAVEGUIDE LAYERS PRODUCED BY TITANIUM DIFFUSION IN LITHIUM NIOBATE.** Ytshak Avrahami, Emil Zolotoyabko, Technion-IIT, Dept of Materials Engineering, Haifa, ISRAEL; Wolfgang Sauer, Till-Hartmut Metzger, Johann Peisl, Sektion Physik, Ludwig-Maximilians Universitat, Munich, GERMANY.

Ti-diffusion at  $1000^\circ\text{C}$  in an oxygen environment is used in fabricating lithium niobate(LiNbO<sub>3</sub>)- based optoelectronic devices in order to increase the refractive index of the near-surface LiNbO<sub>3</sub> layer. An optical barrier to the propagation of light into the crystal bulk arises from replacement 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<sub>3</sub>, and their influence on the structural characteristics of the LiNbO<sub>3</sub> 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). GID in combination with TEM helped us to follow the development and temporal decay of a rutile-like phase,  $(\text{Li}_{0.25}\text{Nb}_{0.75}\text{O}_2)_{1-x}(\text{TiO}_2)_x$ , as well as its orientation relations to the matrix. A new solid state reaction is proposed which clarifies the mechanism of phase transformation and role of cation replacements. By comparison of

HRXRD and SIMS results we were able to relate the depth-resolved profiles of the  $\text{LiNbO}_3$  lattice parameter to the Ti-concentration profiles. It was shown that both techniques can be used with confidence to determine the Ti-diffusion coefficients in  $\text{LiNbO}_3$ . As a result of comparison a numerical factor, K, was obtained which allowed to characterize quantitatively the extent of lattice contraction due to Ti-incorporation in the  $\text{LiNbO}_3$  crystal. The K-factor, which is of crucial importance to waveguide properties, was found to increase with annealing time, indicating a variable strain contribution to the structural parameters of the waveguide layer due to gradual disappearing of the rutile-like phase, observed by GID.

SESSION R9: POSTER SESSION:  
APPLICATIONS OF SYNCHROTRON RADIATION  
TECHNIQUES TO MATERIALS SCIENCE

Chair: Susan M. Mini  
Wednesday Evening, December 1, 1999  
8:00 P.M.  
Exhibition Hall D (H)

**R9.1**

A NEW TRIPLE CRYSTAL DIFFRACTOMETER FOR HIGH ENERGY SYNCHROTRON RADIATION AT THE APS AT ARGONNE NATIONAL LABORATORY. U. Ruett, Materials Science Division at Argonne National Laboratory and Northern Illinois University; M.A. Beno, Materials Science Division at Argonne National Laboratory; J.R. Schneider, Hamburger Synchrotron Strahlungslabor (HASYLAB) at DESY, GERMANY; P.A. Montano, 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 installed at the elliptical multipole wiggler with a critical energy of 32.5 keV. This is the first sophisticated diffractometer for photon energies above 60 keV in the US. In contrast to the other three diffractometers at HASYLAB (Germany) and ESRF (France) this one is operated with a vertical scattering plane, while a horizontally scattering pre-mono-chromator provides the beam. 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 large penetration depths. It offers the opportunity to study samples sub-millimeter to several 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 precise 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 US Department of Energy, Office of Basic Energy Science, Division of Materials Sciences, under contract W-31-109-ENG-38 and the State of Illinois under HECA.

**R9.2**

STRUCTURAL CHARACTERIZATIONS USING SYNCHROTRON RADIATION OF OXIDE FILMS AND MULTILAYERS GROWN BY MOCVD. C. Dubourdieu, J. Lindner, M. Rosina, F. Weiss, J.P. Sénateur, Laboratoire des Matériaux et du Génie Physique, ENSPG, UMR CNRS, St. Martin d'Hères, FRANCE; J.L. Hodeau, J.F. Berar, Laboratoire de Cristallographie, CNRS, Grenoble, France; E. Dooryhee, 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 metal organic chemical vapor deposition (MOCVD). The investigated heterostructures were lacunar manganite  $\text{La}_{0.8}\text{MnO}_3$  film and superlattices of  $(\text{BaTiO}_3/\text{SrTiO}_3)_{15}$  and  $(\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{SrTiO}_3)_{15}$ . Reflectometry measurements were performed (BM 16 beam line) to get information on the quality of film/substrate and film/film interfaces of the heterostructures. The experimental data were compared to simulated spectra. For  $\text{La}_{0.8}\text{MnO}_3$  film deposited on  $\text{SrTiO}_3$ , the roughness is about 0.8 nm (about two unit cells) for a total thickness of 100 nm. For  $(\text{BaTiO}_3/\text{SrTiO}_3)_{15}$  multilayers, the roughness is found to be less than 1 nm. Anomalous diffraction was performed on superlattices of  $(\text{BaTiO}_3/\text{SrTiO}_3)_{15}$  and  $(\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{SrTiO}_3)_{15}$  on CRG-D2AM beam line. This beam line is equipped with a seven circles goniometer. The multilayers are oriented with the 001 direction perpendicular to the substrate plane. Therefore, 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. The satellite peaks observed for both types of multilayers indicate the good coherence over the whole stacking. For the  $(\text{BaTiO}_3/\text{SrTiO}_3)_{15}$  systems, the diffraction peaks are particularly well resolved even for the highest order (008 peak), showing an excellent epitaxial quality. The relative intensities of the satellite peaks change as the incident energy is varied, related to the relative occurrence of strontium in each layer.

**R9.3**

AN EXAFS STUDY OF LOCAL STRUCTURE AND COMPOSITIONAL HOMOGENEITY IN CALCIUM ZIRCONIUM TITANATE SOLID SOLUTION SAMPLES PREPARED USING SOLUTION METHODS. Jie Xu, Angus Wilkinson, Sidhartha Pattanaik, School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA.

Samples of  $\text{Ca}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ( $x = 0, 0.25, 0.5, 0.75, 100$ ) (CZT) were synthesized by four different routes: homogeneous sol-gel, inhomogeneous sol-gel, acetic acid/methanol and ceramic methods. In the inhomogeneous sol-gel procedure, the calcium titanate and calcium zirconate precursor solutions were partially hydrolyzed prior to mixing. The effect of the four processing procedures on the structure of the resulting CZT gels and crystalline products was studied by EXAFS and powder diffraction. Both the Zr K-edge and Ti K-edge data show that (i) EXAFS is sensitive to the local structure around the absorber, in particular the magnitude of the peak corresponding to the nearest neighbor Ti/Zr - Ti/Zr distance shows a strong dependence on the composition of the solid solution; (ii) the low temperature amorphous materials have very different local structures from those found in the crystalline compounds; (iii) the processing chemistry plays a very important role in determining the B-site cation distribution in the solid solution. The inhomogeneous sol-gel method gave a significantly more heterogeneous cation distribution than the other methods. Our data suggest that the cation distribution in CZT can be controlled by manipulating the synthesis procedure.

**R9.4**

EXAFS AND RAMAN STUDIES OF  $\text{PTMG}_n:\text{MCl}_2$  AND  $\text{PTMG}/\text{PEG}_n:\text{MCl}_2$  COMPLEXES ( $\text{M} = \text{Co}, \text{Zn}$ ). C.A. Furtado, Centro de Desenvolvimento da Tecnologia Nuclear-CDTN/CNEN, Belo Horizonte MG, BRAZIL; G. Goulart Silva, A.O. Porto, Universidade Federal de Minas Gerais, Department of Chemistry, Belo Horizonte MG, BRAZIL; R.A. Silva, Universidade Federal de Minas Gerais, Department of Physics, Belo Horizonte MG, BRAZIL; M.C.M. Alves, Laboratório Nacional de Luz Síncrotron - LNLS, Campinas SP, BRAZIL; P. J. Schiling, R. Tiltsworth, Center for Advanced Microstructures and Devices - CAMD, Louisiana State University, Baton Rouge, LA.

Polymer electrolytes are complex systems obtained from the dissolution of salts in a polymer. These systems are used in electrochemical devices, as batteries and capacitors, electrochromic windows and thermoluminescent displays, which construction depends on the availability of different kinds of specific ions. The chemical interactions between the polymeric chain and the ions determine the ionic conduction behaviour. The polymer is preferentially a flexible disordered matrix in which ionic species can move through the free volumes existing in the bulk. The ionic transport occurs only in the amorphous region. Therefore, the understanding of the local structure of these systems should allow a better designing and development of new materials with high technological performance. The local structure around these metal cations can be perfectly investigated by the Extend X-Ray Absorption Fine Structure (EXAFS) technique, which gives information about the number of neighbours, distances and thermal/static disorder. Raman spectroscopy gives information about the ion-ion and ion-polymer interaction. In this work, EXAFS and Micro-Raman spectroscopy measurements have been performed in a series of liquid polymer electrolytes prepared using poly(tetramethylene glycol) (PTMG) and poly(tetramethylene glycol)/poly(ethylene glycol) (PTMG/PEG) copolymer as matrix and  $\text{ZnCl}_2$  or  $\text{CoCl}_2$  as dopant, in the concentration range of  $n = 30$  to 90 ( $n$  is the Oxygen/Metal cation molar ratio). The EXAFS results showed the presence of Co-O and Co-Cl coordination shells for PTMG/ $\text{CoCl}_2$  and PTMG/PEG/ $\text{CoCl}_2$  systems. The Zn-based systems studied presented only Cl as neighbour in the studied concentration range. The presence of  $\text{ZnCl}_2$  species was evidenced in the Raman spectra by a band in  $306 \text{ cm}^{-1}$ , which intensity increases with the increase of the salt concentration. This band is characteristic of the Cl-Zn-Cl stretching of the  $\text{ZnCl}_2$  species in aqueous solution.

**R9.5**

SYNCHROTRON SMALL ANGLE X-RAY SCATTERING OF MELT CRYSTALLIZED POLYMERS. Georgi Georgiev, Patrick S. Dai, Elizabeth Oyebode, Peggy Cebe, TUFTS University, Dept. Physics and Astronomy, Medford, MA; Malcolm Capel, Brookhaven

National Laboratory, Biology Dept., Upton, NY.

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(etheretherketone), PEEK, and its blends with 20wt-% 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 different levels 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 invariant, and linear stack crystallinity. These parameters are strongly affected by the addition of PEI to PEEK, and also change systematically during thermal treatment. Results are consistent with an interlamellar placement for PEI. We find no evidence for formation of large amorphous pockets for either treatment scheme.

#### R9.6

**SPECTROSCOPIC CHARACTERISATION OF MIXED TITANIA-SILICA OXIDE CATALYSTS PREPARED BY THE SOL-GEL ROUTE.** Mark A. Holland, David M. Pickup, Robert J. Newport, Gavin Mountjoy, School of Physical Sciences, University of Kent at Canterbury, Canterbury, UK.

Mixed titania-silica oxides are of contemporary importance because of their potential applications as catalysts and catalytic supports, ultra-low expansion glasses and anti-reflective thin film coatings. A number of mixed titania-silica oxides of the general formula  $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ , have been prepared via the sol-gel route. They have been tested for their catalytic effectiveness using the epoxidation of cyclohexane as a test reaction. The gels were subjected to various drying conditions, including washing in low surface tension solvents to preserve pore structure, and hence to maximise catalytic activity. The effect of calcination temperatures and the associated rate of heating in this context was also investigated. Extensive synchrotron X-ray and complementary characterisation was performed on the samples, including the use of XANES, EXAFS, UV-vis. and FT-IR spectroscopy. Cryopometric measurements have also been taken in order to measure pore size distribution. The data from these techniques has revealed that the catalytic activity is dependant upon the number of Ti-O-Si linkages (i.e. upon the Ti dispersion within the network), surface area, and the co-ordination number of Ti in the network. This work illustrates the way in which several spectroscopic techniques, including synchrotron related experiments, may coherently be used in order to determine a structural picture of the material and relate it to macroscopic catalytic properties.

#### R9.7

**XAS AND XPS CHARACTERIZATION OF DIESEL EXHAUST PARTICULATES.** Art J. Nelson, James L. Ferreira, John G. Reynolds, Lawrence Livermore National Laboratory, Livermore, CA; Joseph W. Roos, Ethyl Corporation, Richmond, VA.

We have characterized particulates from a 1993 11.1 Detroit Diesel Series 60 engine with electronic unit injectors operated using fuels with methylcyclopentadienyl manganese tricarbonyl (MMT) and overbased calcium alkylbenzene sulfonates added. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) spectroscopy, X-ray photoabsorption (XAS) spectroscopy and X-ray photoemission (XPS or ESCA) spectroscopy were used to comprehensively characterize the diesel particulates. Results reveal a mixture of primarily Mn-oxide with some Mn-phosphate, and Ca-sulfate with possibly some Ca-phosphate on the surface of the filtered particulates from the diesel engine.

#### R9.8

**SURFACE INDUCED LAYERING IN LIQUID METALS AND ALLOYS.** E. DiMasi, B.M. Ocko, Physics Dept., Brookhaven National Laboratory, Upton, NY; H. Tostmann, O.G. Shpyrko, P.S. Pershan, Dept. of Engineering and Applied Sciences, Harvard University, Cambridge MA; M. Deutsch, Physics Dept., Bar-Ilan University, ISRAEL.

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 charged ion cores screened by a conduction electron sea, is governed by complicated interionic interactions which are not addressed by theories of simple liquids. The screened Coulomb

potential governing the bulk liquid metal gives way at the surface to 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-Bi, and on the temperature dependent solubility of Au in Hg, the first atomic scale structural studies available for such systems. We discuss the application of this technique to in-situ studies of reactions and catalysis at the liquid metal surface.

#### R9.9

**GROWTH TWINS IN  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_3(\text{BO}_3)_4$  AND  $\text{Nd}_x\text{Gd}_{1-x}\text{Al}_3(\text{BO}_3)_4$  CRYSTALS OBSERVED BY WHITE-BEAM SYNCHROTRON RADIATION TOPOGRAPHY.** Xiaobo Hu, Jiyang Wang, Ming Guo, Shanrong Zhao, Bo Gong, Jingqian Wei and Yaogang Liu, State Key Laboratory of Crystal Materials, Shandong University, Jinan, P. R. CHINA.

Growth twins in  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_3(\text{BO}_3)_4$  and  $\text{Nd}_x\text{Gd}_{1-x}\text{Al}_3(\text{BO}_3)_4$  crystals were observed by white-beam synchrotron radiation topography combined with chemical etching method. It has been found that the growth twins in  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_3(\text{BO}_3)_4$  crystals are of inversion types in which two twinned pairs have the central inversion relationship, whereas the growth twins in  $\text{Nd}_x\text{Gd}_{1-x}\text{Al}_3(\text{BO}_3)_4$  crystals are of  $180^\circ$  rotation types in which the twofold symmetric operation axis is parallel to the [0001] axis. The inversion twins in  $\text{Yb}_x\text{Y}_{1-x}\text{Al}_3(\text{BO}_3)_4$  crystals are visible in x-ray topography not by 'domain contrast' but by 'boundary contrast' stemming from the kinematical x-ray diffraction at the boundary. However, the rotation twins in  $\text{Nd}_x\text{Gd}_{1-x}\text{Al}_3(\text{BO}_3)_4$  crystals often show black-and-white contrast in x-ray topography originating from the different structure factors between two twinned pairs. In addition, the formation mechanisms of twins are discussed.

#### R9.10

**LOCAL STRUCTURE PARAMETERS OF THIN FILMS AND ORDERED Ge NANOCLESTERS IN Si- MATRIX BY XAFS SPECTROSCOPY.** S.B. Erenburg, N.V. Bausk, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; N.P. Stepina, 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% larger 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 GeK EXAFS data using EXCURV92 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  $0^\circ$  and  $90^\circ$  between the normal of the Si(001) plane and the electric field vector to determine structural parameters anisotropy. Two structures were formed in parallel on two part of Si(001) substrate. Both type of structure composed of three Ge/Si bilayers. The first type of the structure 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  $\sim 15\text{nm}$  and high  $\sim 1.5\text{nm}$ . The local microstructure parameters (interatomic distances, Ge coordination numbers and their anisotropy) were linked to nanostructures morphology and adequate models were suggested and discussed. In particular, it was established 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.

#### R9.11

**X-RAY SPECTROSCOPIC STUDY OF THE TRANSFORMATION OF ULTRA DISPERSED DIAMOND TO CARBON ONION PARTICLES.** A.V. Okotrub, L.G. Bulusheva, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; V.L. Kuznetsov, Yu.V. Butenko, A.L. Chuvilin, Borekov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA.

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

Measured spectra were compared to the C<sub>Kα</sub> spectra of the initial UDD sample and the nontextured graphite. C<sub>Kα</sub> spectrum of the onion-like particles produced 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 C<sub>Kα</sub> spectra was performed on the basis of quantum-chemical calculations of series of carbon networks having the various number of and kind of the topological defects.

#### **R9.12**

**ANGLE DEPENDENCE OF X-RAY FLUORESCENCE YIELD AND ELECTRONIC STRUCTURE OF MULTIWALL CARBON NANOTUBES.** L.G. Bulusheva, A.V. Okotrub, A.V. Gusel'nikov, A.V. Antich, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA.

High-resolution C<sub>Kα</sub> spectra have been obtained for the samples containing carbon cage particles synthesized using the arc-discharge graphite evaporation technique. Inner part of the cathode deposit contains of 90 percents of multiwall carbon nanotubes (MWNT). C<sub>Kα</sub> spectrum of MWNT is similar to that of polycrystal graphite. The dependence of the spectral profile on the geometry was investigated using quantum-chemical calculations of the carbon nanotube fragments with different helical pitch. The spectrum of multiwall particles was found to agree best with the theoretical spectra of zig-zag tubes. X-ray emission of textured graphite has the angle dependence, that makes possible to share the sigma- and pi-electron contribution to the valence band. Yield of fluorescence from the sample of MWNT was measured for five orientation of the sample relative to the direction of X-ray emission. The difference between C<sub>Kα</sub> spectra of nanotubes is less than that in the case of graphite. C<sub>Kα</sub> 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-valence electrons for the carbon nanotubes has good correlation with the X-ray emission experimental data.

#### **R9.13**

**THE INVESTIGATION OF THE FAST STRUCTURAL CHANGES IN THE TECHNOLOGICAL PROCESSES (RAPID HEATING, COOLING, CHEMICAL AND PHASE TRANSFORMATION) WITH THE MICROSECOND TIME RESOLUTION.** Boris Tolochko, Nikolay Lyakhov, Boris Bokhonov, Institute of Solid State Chemistry, Dept of Synchrotron Radiation, Novosibirsk, RUSSIA; Vladimir Aulchenko, Institute of Nuclear Physics, Dept of High Energy Physics, Novosibirsk, RUSSIA.

In Institute of a Nuclear Physics the unique one-coordinate detector OD-3 for synchrotron radiation (SR), was designed for X-ray diffraction (see V.M.Aulchenko, J. Synchrotron Radiation, 1998, 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 WAXS and SAXS experiments. Now this detectors are using in Photon Factory (KEK, Japan), Spring-8 (Japan) and VEPP-3 (Russia) at four SR beam lines. The detector was used for examination of the fast structural changes during technological processes, such as a heating (or cooling) with velocity 100000 deg/sec, electrochemical reactions, solid state reactions, gasless combustion synthesis, photochemical reactions. During experiments at SR beam lines the samples was in a reactors with controlled medium (high vacuum, or 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 quasicrystal - 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 Tolochko, Institute of Solid State Chemistry, Dept of Synchrotron Radiation, Novosibirsk, RUSSIA; Mike Fedotov, Gennady Kulipanov, Pavel Logachev, Nikolay Mezentsev, Svyatoslav Mishnev, 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 field impact (see B.P.Tolochko, et al, Moving source: the idea of the nanosecond time resolution diffraction experiments, Preprint BINP no 99-20, Novosibirsk, 1999; and the same in the NIM

in press). The fast change of orbit of electrons results in displacement of a beam of synchrotron radiation. The parallel displacement of synchrotron radiation beam happens 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 positional sensitive X-ray detectors we received diffraction patterns with a time resolution equal to time between electrons bunches (250 nsec on VEPP-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 made theoretical estimations which shown a practical capability, of the scheme, which will allow to execute a beam scanning of synchrotron radiation with speed near 10000 km/s 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. Mini  
Thursday Morning, December 2, 1999  
Suffolk (M)

#### **9:00 AM R10.1**

**HIGH-RESOLUTION STRUCTURAL ANALYSIS OF THE Te/Ge(001) SURFACE.** Osami Sakata, Northwestern Univ, Paul F. Lyman, Univ of Wisconsin-Milwaukee, Brad P. Tinkham, Don A. Walko, Northwestern Univ, Michael J. Bedzyk Northwestern Univ and Argonne National Lab.

Surface structures formed by the adsorption of Te on Ge(001) were studied with X-ray standing wave and x-ray scattering measurements. The latter took place at a newly commissioned surface science chamber / diffractometer at the Advanced Photon Source. At a coverage of 1 ML, Te is adsorbed at the bridge site in a (1x1) arrangement, as expected. However, at 0.5 ML a new surface structure is formed in which Te-Ge heterodimers make up a c(2x2) 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 to ANL, and by the NSF under contract No DMR-9632593, and No DMR-9632472 to the MRC at NU.

#### **9:15 AM R10.2**

**THIN-FILM X-RAY STANDING WAVES - A NEW STRUCTURAL PROBE FOR FERROELECTRIC THIN FILMS.** A. Kazimirov, Northwestern U., M.J. Bedzyk, NU, Argonne National Lab, T.-L. Lee, NU, D.L. Marasco, NU, ANL, O. Auciello, ANL, C. Thompson, Northern Illinois U., ANL, K. Ghosh, NIU, ANL, S.K. Streiffer, ANL, G.R. Bai, ANL, G.-B. Eom, Duke U.

A new method for microscopically determining the polarity of epitaxial ferroelectric thin films has been developed. The method is based on the weakly 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 dynamical 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 PbTiO<sub>3</sub> film has a reflectivity of ca. 10<sup>-4</sup> leading to V ≈ 10<sup>-2</sup>. 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' PbTiO<sub>3</sub> thin films and to observe polarity switching in Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> (PZT) capacitors. Work supported by the US DOE under contract No W-31-109-ENG-38 to ANL, and by the NSF under contract No DMR-9632593, and No DMR-9632472 to the MRC at NU.

#### **9:30 AM \*R10.3**

**INELASTIC NUCLEAR RESONANT SCATTERING STUDIES OF PHONONS IN ALLOYS.** Brent Fultz, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

Nuclear resonant  $\gamma$ -ray scattering is usually performed by using the Mossbauer effect. For the past decade, such 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 measure nuclear resonance scattering accompanied by phonon creations and annihilations [2]. The present inelastic experiments are incoherent; in the case of <sup>57</sup>Fe a 6 keV internal

conversion x-ray from the sample is detected. The measured inelastic spectra are analyzed to provide a phonon partial density of states of  $^{57}\text{Fe}$  in the sample, using procedures nearly identical to those for inelastic incoherent neutron scattering. The phonon partial DOS is the projection at the  $^{57}\text{Fe}$  atom of the phonon polarization intensity. It provides a local viewpoint on how the  $^{57}\text{Fe}$  atoms vibrate. We have been using inelastic nuclear resonant scattering to study vibrations in alloys with various states 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  $^{57}\text{Fe}$  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 for measurements on chemically disordered, partially-ordered and ordered  $\text{Fe}_3\text{Al}$  [4] and  $\text{Pt}_3\text{Fe}$  alloys. Chemical order in these alloys was characterized thoroughly by conventional Mössbauer spectrometry and by x-ray diffractometry. The phonon partial DOS's of  $^{57}\text{Fe}$  in these alloys show a strong dependence on 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 first nearest neighbor shells. [1] T.S. Toellner, et al. APL 71, 2112 (1997). [2] M. Seto, et al., PRL 74, 3828 (1995). W. Sturhahn, et al. PRL 74, 3832 (1995). [3] Fultz, et al., PRL 79, 937 (1997). [4] Fultz, et al., PRL 80, 3304 (1998).

SESSION R11: THERMOELECTRIC AND  
MAGNETIC MATERIALS: X-RAY  
PHOTOEMISSION, STANDING WAVES 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  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ . M.V. Zimmermann, J.P. Hill, Doon Gibbs, M. Blume, Dept of Physics, Brookhaven National Laboratory, NY; D. Casa, B. Keimer, Dept of Physics, Princeton University, NJ; Y. Murakami, Photon Factory, Tsukuba, JAPAN; Y. Tomioka, Joint Research Center for Atom Technology, Tsukuba, JAPAN; Y. Tokura, Department of Applied Physics, University of Tokyo, JAPAN.

It has recently been possible to directly observe the charge valence and orbital ordering in manganite materials through the use of resonant x-ray scattering [1]. The sensitivity for orbital ordering arises from a splitting of the Mn 4p 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  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  sites, leading to anomalous scattering at the difference reflection. We used these techniques to investigate the interplay of charge and orbital ordering in  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x = 0.4$  and  $x = 0.5$  and detected that below a common transition temperature of  $T_O = 245$  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 fluctuations 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. Murakami *et al.* Phys. Rev. Lett. **80**, 1932, (1998).

**11:00 AM R11.2**

BAND STRUCTURE OF Ni(100) VERSUS PERMALLOY(100). N.Franco, T. Van Buuren, C. Bostedt, L. Terminello, Lawrence Livermore National Laboratory, Livermore, CA; F.J. Himpsel, Department of Physics, University of Wisconsin Madison, Madison, WI.

The magnetic characteristics of permalloy ( $\text{Ni}_{0.8}\text{Fe}_{0.2}$ ) make this a material widely used in data storage technology. Sensors for hard disk reading heads have been using anisotropic magnetoresistance (AMR) of permalloy or giant magnetoresistance (GMR) of permalloy/Cu/Cu thin films. It also exhibits an unusually-short scattering length for 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 beam line. Using the appropriate photon energies we are able to probe the high symmetry points in k-space at  $\Gamma(400)$  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 the electronic and magnetic properties, particularly regarding possible minority spin scattering states. [1] D.Y. Petrovykh, et al., Appl. Phys. Lett. **73**, 3459 (1998). N. Franco is support by the Spanish Education and Culture office under a F.P.I. contract PF-98-33501134. 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 RESOLUTION ANGLE RESOLVED PHOTOEMISSION STUDIES OF THE TEMPERATURE DEPENDENT ELECTRONIC STRUCTURE OF THERMOELECTRIC MATERIALS.

D.N. McIlroy, D. Zhang, Y. Kranov, B. Kempton, University of Idaho, Dept. of Physics, Moscow, ID; T.M. Tritt, R.T. Littleton, Clemson University, Dept. of Physics, Clemson, SC; C.G. Olson, Ames Laboratory, Ames, IA.

$\text{ZrTe}_5$  and  $\text{HfTe}_5$  are 2D layered systems where the layers interact via van der Waals like bonds. Both samples have two states within 0.5 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 temperature  $s$  which corresponded to the peaks in the bulk resistivities of  $\text{ZrTe}_5$  and  $\text{HfTe}_5$ , 170 K and 80 K, respectively. At the  $\text{ZrTe}_5$  transition temperature, the two states near the Fermi level shift closer together as well as towards the Fermi level. Similar shifts of the corresponding bands of  $\text{HfTe}_5$  at elevated temperatures were less obvious. We attribute this in part to the extremely small size of the Fermi surface of  $\text{HfTe}_5$  ( $0.150 \text{ \AA}^{-1}$ ) which makes it difficult to observe the phenomena. These results suggest that the magnitude of the effects observed for  $\text{ZrTe}_5$  may scale with Fermi surface size, or transition temperature, or a combination of both. The effects of doping on the properties of  $\text{ZrTe}_5$  and  $\text{HfTe}_5$  will also be addressed.

SESSION R12: X-RAY ABSORPTION  
SPECTROSCOPY OF MAGNETIC MATERIALS  
AND NANOPARTICLES I

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

**1:30 PM R12.1**

PHASE TRANSITION IN  $\text{MnF}_2$ - $\text{CaF}_2$  SUPERLATTICES AND DOUBLE HETEROSTRUCTURES EPITAXIALLY GROWN ON Si(111). Hironori Ofuchi, Masao Tabuchi, Yoshikazu Takeda, Dept. of Materials Science and Engineering, Graduate School of Engineering Nagoya Univ., Nagoya, JAPAN; Alexander G. Banskchikov, Nikolai S. Sokolov, Nikolai L. Yakovlev, Ioffe Physico-Technical Inst., Russian Academy of Sciences, St. Petersburg, RUSSIA.

Attractive optical and magnetic properties of rutile type structure  $\text{MnF}_2$  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  $\text{MnF}_2$  layers, which are attractive for basic studies and have important potential applications. Epitaxial  $\text{MnF}_2$  has a possibility to form a cubic structure when grown on cubic  $\text{CaF}_2$ . In this work,  $\text{MnF}_2$ - $\text{CaF}_2$  superlattices (SLs) and double heterostructures (DHSs) on Si(111) were investigated by fluorescence EXAFS using synchrotron radiation in order to find the coherency of  $\text{MnF}_2$  crystal structure sandwiched by fluorite  $\text{CaF}_2$  layers. The  $\text{MnF}_2$ - $\text{CaF}_2$  SLs and DHSs were grown by MBE on Si(111) with  $\text{CaF}_2$  buffer layer. The  $\text{MnF}_2$ - $\text{CaF}_2$  SLs consist of 15 periods. All the samples were capped by  $\text{CaF}_2$  layer. RHEED measurements during the growth showed that the first 3ML of  $\text{MnF}_2$  on Si substrate grew 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 (2.12-2.17Å) and the longer one (2.25-2.31Å) in each sample, but different content ratios. The shorter Mn-F bond length was close to the average of the Mn-F bond lengths in rutile-type  $\text{MnF}_2$ . The longer Mn-F bond length was close to the Mn-F bond length (2.28Å) in fluorite-type  $\text{MnF}_2$ . The EXAFS analysis also revealed that in thin  $\text{MnF}_2$  layers ( $\leq 3\text{ML}$ ) the fluorite structure which does not exist at normal condition prevailed over the rutile structure, and the content ratio of the fluorite  $\text{MnF}_2$  strongly depended on the thickness of the  $\text{MnF}_2$  layer. Therefore, thin  $\text{MnF}_2$  layers coherently grew in fluorite structure on  $\text{CaF}_2$  and changed to

the rutile structure with the increase of MnF<sub>2</sub> layer thickness. The phase transition dependences of ESR line shapes and CL 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 Cu<sub>100-x</sub>Fe<sub>x</sub> (x = 50-80), the XANES analysis indicates that throughout this region the two coexistent phases have almost identical composition, consistent with that of the overall mixture. This represents a novel two-phase coexistence representing a region of overlap in solubility rather than the normal miscibility gap.

**2:00 PM \*R12.3**

EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDIES OF DOPED La-MANGANITES: THE ROLE OF DISORDER IN COLOSSAL MAGNETORESISTANCE. V.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 La-manganites in the presence of an applied magnetic field can exceed 1,000,000%. This unusually large magnetoresistance (a.k.a. colossal magnetoresistance (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 concentration. In order to explore the role of disorder in the CMR of these materials we have employed ion irradiation to systematic damage the lattice of La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> thin films. Extended x-ray absorption fine structure (EXAFS) analysis of the damaged films is performed using FEFF simulations, cumulant expansion, and the ratio method. We find that low radiation doses, expected to result in a small amount of lattice damage, in fact leads to large local distortions around the Mn cations that lead to a drop in the PI-FM transition temperature from 240K to full suppression, and an increase in the magnetoresistance from 600% to > 2,000,000%. It appears that the irradiation serves the role of a perturbation, allowing for significant alteration of the samples' electronic properties. A broader view of the literature reflects that 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 reported 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. Philippe Dillmann, LPS DRECAM CEA, CE Saclay, Gif Sur Yvette, FRANCE; Belkacem Regad, Université de Technologie de Compiègne, Compiègne Cedex, FRANCE; Gerard Moulin, Université de Technologie de Compiègne, Compiègne Cedex, FRANCE.

The further development of new coal-gasification fired power stations needs to study the behaviour of stainless steels in specific conditions 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 (H<sub>2</sub>O, H<sub>2</sub>S, CO, CO<sub>2</sub>) containing corrosive ashes with a high proportion of vanadium. 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 developed on these steels. The assessment of synchrotron radiation sources gave rise to new studies on small samples with dimensions going down to few μm<sup>3</sup>. Meanwhile focusing optics like capillary, bended mirrors, Bragg Fresnel and refractive lenses have been improved and now take advantage of the brilliance of these new X-ray sources. Thus, we managed micro XANES experiments with the ESRF 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.

SESSION R13: X-RAY ABSORPTION SPECTROSCOPY OF MAGNETIC MATERIALS AND NANOPARTICLES II

Chair: Stephen R. Wasserman  
Thursday Afternoon, December 2, 1999  
Suffolk (M)

**3:15 PM R13.1**

ELECTRONIC STRUCTURE OF Ge-NANOCUSTER FILMS PROBED WITH SYNCHROTRON RADIATION. C. Bostedt, Universitat Hamburg, Hamburg, GERMANY and Lawrence Livermore National Laboratory, CA, T. v.Buuren, N. Franco, M. Balooch and L.J. Terminello, Lawrence Livermore National Laboratory, Livermore, CA; T. Moller, Hasylab 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 confinement theory. The blueshift ranges from 0.2eV to 0.4eV for clusters between 4nm and 2nm. No oxygen features are visible in XAS and XPS. Preliminary photoemission data taken on clusters in the range from 7-9nm does not show any valence band shifts, as these structures are too big for confinement effects. 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 Ge-clusters is much larger for clusters of the same size. Effective mass calculations of Si and Ge clusters confirm this effect. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

**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 local bonding 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. Research supported by DOE grant no. DE-FG02-97ER45662. XAS measurements made at SSRL, which is funded by the DOE Office of Basic Energy Sciences and the NIH Biotechnology Resource Program.

**3:45 PM R13.3**

THIOL-CAPPED GOLD NANOPARTICLES: STRUCTURE AND SELF-ASSEMBLED SUPER-CRYSTALS. Daniela Zanchet, Lab. Nac. de Luz Síncrotron, Campinas-SP, BRAZIL; Hélio Tolentino, Lab. Nac. de Luz Síncrotron, Campinas-SP, BRAZIL; Blair D. Hall, Measurement Standards Lab., Industrial Res. Ltd, Lower Hutt, NEW ZEALAND; Daniel Ugarte, Lab. Nac. de Luz Síncrotron, Campinas-SP, BRAZIL.

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 thiol-passivated gold nanoparticles (2 - 4 nm) such as: inter-atomic

distance contraction and structure population (fcc, decahedron and icosahedron). A slight inter-atomic distance reduction was observed (< 1%) as a function of particle diameter, but for small sizes it was less than the one expected in free clusters. A short metal-ligand bond was also revealed indicating a rather strong surface interaction that would partially compensate the expected contraction. Structure type population was based on powder X-ray diffraction, where a fitting procedure was implemented considering size dispersion and different structures; a high percentage of imperfect or more complex nanoparticle structures was deduced. Self-assembled nanoparticle super-crystals were also studied, and a soft thermal treatment was used to enhance particle ordering. In particular, an anomalous packing was observed in thin nanoparticle films composed by a few layers (1-3) where the first one lying on the amorphous carbon substrate is expanded and the second layer formed ordered regions (micron size) with particles sitting on two-fold saddle points.

#### 4:00 PM R13.4

REAL-TIME STUDY OF GRAIN GROWTH IN NANOCRYSTALLINE MATERIALS USING SYNCHROTRON RADIATION. C.E. Krill, University of the Saarland, Dept of Physics, Saarbruecken, GERMANY; H. Natter, University of the Saarland, Dept of Chemistry, Saarbruecken, 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  $\langle D \rangle$ , which for conventional samples ( $\langle D \rangle \geq 1 \mu\text{m}$ ) involves optical microscopy of planar sections passing through a bulk specimen. Such sample preparation is destructive in nature, and the subsequent processing of microscopy images necessary to obtain the average grain size and size distribution is usually quite time consuming, even with the help of modern image-analysis software. The recent development of synthesis techniques for nanocrystalline materials ( $\langle D \rangle \leq 100 \text{ nm}$ ) has brought with it the possibility to study grain growth by means of 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 BM16 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 of the growth kinetics on  $\langle D \rangle$ —a hypothesis 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

Chairs: Debra R. Rolison 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; L. Soderholm, Daniel M. Giaquinta, 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 uranyl 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 surface using thin self-assembled organic films 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 zeolites and variable for the smectites. 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 validate 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 W31-109-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, Seaborg Institute, Lawrence

Livermore National Laboratory, Livermore, CA.

We have investigated the interaction of the actinyl ion,  $\text{UO}_2^{2+}$ , 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 surface complex structure determination. Details of the approaches to XAFS analysis in these systems will be discussed. In acid solution ( $\text{pH} \sim 3.5$ ), the uranyl ion shows a strong interaction with the silica and alumina surfaces, and a relatively 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 structure of a free uranyl aquo complex. Based on this formalism, surface complexation on silica and alumina occurs through an inner-sphere mechanism with surface oxygen atoms binding directly to the equatorial region of the uranyl ion. In contrast, sorption on montmorillonite occurs by 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 ( $\text{pH} \sim 6$ ), sorption on all of 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.

Antonio, Chemistry Division, Argonne National Laboratory, Argonne, IL; Monica Lee Tischler and Michael Mardos, Benedictine University, Lisle, IL.

Desulfovibrio desulfuricans (DSV) is an anaerobic sulfate-reducing bacterium that is also known to change the oxidation state of iron during the course of its growth. Although iron redox couples can sometimes be used for energy, sulfate is available as the electron acceptor in these experiments. The reduction of iron under 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) ( $\text{O}=\text{Np}=\text{O}$ )<sup>+</sup> moiety. Its reduction to tetravalent 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. Varlot, M. Kasrai, J.M. Martin, B. Vacher, G.M. Bancroft, G. DeStasio, E.S. Yamaguchi, P.R. Ryason.

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 dialkyldithiophosphates (ZDDPs) have been widely used as antioxidant and antiwear additive since the 40s. The demand for reduction of phosphorous/sulphur content in engine oils has forced the oil suppliers to modify the formulation of lubricant 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 characterise the protective layers formed by lubricant additives. 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. This applies to several fields, 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 tribochemical films. Chemical imaging using the MEPHISTO microscopy beamline was performed to determine the distribution of different species created under rubbing. This will help to understand the mechanisms of formation of the tribochemical films and the interactions between borate additives and ZDDP.

#### 10:30 AM R14.5

##### EXTRACELLULAR IRON-SULFUR PRECIPITATES FROM GROWTH OF *DESULFOVIBRIO DESULFURICANS*.

Mark R. Antonio, Chemistry Division, Argonne National Laboratory, Argonne, IL; Monica Tischler, Dana Witzcak, 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, H<sub>2</sub>S. Ultrafine precipitates that form as a result of abiotic chemical reactions involving H<sub>2</sub>S and adventitious iron or as byproducts of microbial activity can 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 *Desulfovibrio 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 geothermal habitats 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. Isaacs, Department of Applied Science, Brookhaven National Laboratory, Upton, NY.

X-ray absorption and fluorescence techniques employing synchrotron light have been used 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 Al in air but was reduced on air exposure of 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 monitor iron, chromium, and nickel concentrations in solution and in salt layers. Their solubility and relative diffusion 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-AC02-98CH10886.

#### 11:00 AM \*R14.7

IN SITU XAFS CHARACTERIZATION OF INTERMETALLIC AND METAL OXIDE INSERTION ELECTRODES FOR LITHIUM ION BATTERIES. A. Jeremy Kropf, Christopher S. Johnson, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Modern synchrotron x-ray sources have opened up new possibilities for in situ materials characterization for processes that take from minutes to hours to complete. Time-resolved spectroscopy measurements in the past have depended on specialized hardware. However, at third generation x-ray sources, general purpose spectroscopy stations are capable of slow 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 layered Li<sub>x</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> electrode 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 Cu<sub>6</sub>Sn<sub>5</sub> intermetallic insertion electrode.

#### 11:30 AM R14.8

##### EXAFS-DERIVED AMORPHOUS STRUCTURES IN RUTHENIUM OXIDE: IMPLICATIONS FOR CHARGE STORAGE MATERIALS.

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Hydrous ruthenium oxide (RuO<sub>2</sub>·xH<sub>2</sub>O or RuO<sub>x</sub>H<sub>y</sub>) 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 RuO<sub>2</sub>·xH<sub>2</sub>O 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 ruthenia structure increases from 0 to 2.3. Anhydrous RuO<sub>2</sub> has the rutile structure comprising chains of RuO<sub>6</sub> octahedra linked in three dimensions, while the structure of RuO<sub>2</sub>·0.3H<sub>2</sub>O is rutile-like at the RuO<sub>6</sub> core, but less connected and progressively disordered beyond the RuO<sub>6</sub> core. The structure of RuO<sub>2</sub>·2.3H<sub>2</sub>O is composed of chains of disordered RuO<sub>6</sub> octahedra that exhibit no chain-to-chain linking or three-dimensional order. Although the local structures of RuO<sub>2</sub>·0.3H<sub>2</sub>O and RuO<sub>2</sub>·2.3H<sub>2</sub>O 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 tools (such as preparation of hydrous ruthenium oxide as a nanoscale mesoporous material) and physicochemical analyses permits interpretation of charge storage mechanisms in the technological material.

#### 11:45 AM R14.9

##### SYNCHROTRON-BASED STUDIES OF TRANSITION METAL

INCORPORATION INTO SILICA-BASED SOL-GEL MATERIALS. Kevin Mountjoy, Dave M. Pickup, Mark A. Holland, Robert J.

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The sol-gel preparation method provides a convenient route for the preparation of novel mixed-oxide materials. One such group of materials are SiO<sub>2</sub>-based xerogels incorporating TiO<sub>2</sub> and ZrO<sub>2</sub>, with metal oxide contents from 5 to 40mol%. These materials have potentially useful optical and catalytic properties. Their structures are also interesting because Ti and Zr are not compatible elements in an SiO<sub>2</sub> 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 TiO<sub>n</sub> and ZrO<sub>n</sub> groups are accommodated by the SiO<sub>2</sub> 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 SiO<sub>2</sub> network at low concentrations, and phase separation of metal oxide at high concentrations. Although TiO<sub>2</sub>- and ZrO<sub>2</sub>-SiO<sub>2</sub> xerogels show similar trends, there are important differences reflecting the different atomic properties of Ti and Zr.