

Workshop on X-Rays and NanoScience

December 14 - 15, 2000

Argonne National Laboratory

December 14 (Thursday)

9:00 am **Introduction & Opening Remarks** by Gopal Shenoy

Hard X-ray Nano-focusing and Imaging **Chair: Dr. Jörg Maser**

9:10 am **Dr. Barry Lai** (Argonne National Laboratory)
Techniques and Potentials of a Hard X-Ray Nanoprobe

9:35 am **Prof. Arthur M T. Motta** (Pennsylvania State University)
Study of the Microstructure of Zr Alloys and Oxides for Nuclear Applications

10:00 am **Dr. Paul Evans** (Lucent)
Future Directions in Materials Physics with an X-ray Nanoprobe

10:25 am **break**

11:45 am **Dr. Gene Ice** (ORNL)
Frontiers of Nanodiffraction with Synchrotron Radiation

11:10 am **Dr. Robert M. Suter** (Carnegie-Mellon University)
Microstructure of Polycrystalline Materials and Fluid Wetting of Solid Surfaces

11:35 pm **discussion**

12:00 pm **Lunch** (box lunch available with registration \$8.00)

Hard X-ray Scattering **Chair: Dr. Randy Winans**

2:00 pm **Prof. Michael J. Bedzyk** (Northwestern University)
X-ray Standing Wave and Scattering Studies of Nanostructures

2:25 pm **Dr. Wojtek Dmowski** (University of Pennsylvania)
*Local Atomic Order Investigated by the Pair Distribution Function
Obtained from X-ray and Neutron Scattering*

2:50 pm **Dr. Esen Alp** (Argonne National Laboratory)
What can High Energy Resolution X-ray Scattering Offer for Nanoscale Science

3:15 pm **Dr. Jan Hessler** (Argonne National Laboratory)

New Detectors for Time Resolved SAXS Measurements

3:40 pm **discussion**

4:00 pm **break**

Soft Materials **Chair: Dr. Brian Stephenson**

4:20 pm **Prof. Chris Jacobsen** (State University of New York at Stonybrook)
Soft Matter Nanoscience: Soft X-ray Focusing and Spectromicroscopy on Biological and Environmental Specimens

4:45 pm **Dr. Gayle Woloschak** (Argonne National Laboratory)
NANO-TITANS: Interactions of TiO₂ Nanoparticles Bound to Oligonucleotides with Nucleic Acids and Introduction into Mammalian Cells

4:10 pm **Dr. Ian McNulty** (Argonne National Laboratory))

4:35 pm - 5:00 pm **discussion**

December 15 (Friday)

Magnetism **Chair: Dr. Jeff Eastman**

9:00 am **Dr. Mike Fitzsimmons** (Los Alamos National Laboratory)
Asymmetric Magnetization Reversal in Exchange Bias Systems

9:25 am **Dr. John Freeland** (Argonne National Laboratory)
Exploring Magnetic Nanostructures with Polarized X-rays

10:50 am **Dr. George Srajer** (Argonne National Laboratory))
Magnetic Imaging with a Circularly Polarized Microprobe

10:15 am **Dr. Jeff B. Kortright** (Lawrence Berkeley National Laboratory)
Soft X-ray Techniques to Study Magnetic Nanostructures

11:05 am **discussion**

Dr. Barry Lai (Argonne National Laboratory)
Techniques and Potentials of a Hard X-Ray Nanoprobe

X-ray microprobe had found exciting applications in materials science, microelectronics, environmental, and biomedical science. By extending the spatial resolution into the nanoscale regime, x-ray nanoprobe provides essential characterization of nano-materials and -devices. Various contrast mechanisms will allow the mapping of density, elemental composition, crystallographic phase, strain, texture, chemical state, atomic arrangement, magnetization, and polarization. By developing full-field imaging capability and sample environmental chamber, many processes can be studied in-situ under extreme temperatures.

Prof. Arthur M. T. Motta (Pennsylvania State University)
Study of the Microstructure of Zr alloys and oxides for nuclear applications

Zirconium alloys used for nuclear fuel cladding are subjected to a very severe environment during reactor exposure. At the end of life, cladding will have seen 10 to 20 displacements per atom caused by fast neutron irradiation, high temperatures and high corrosion potentials for three years for normal discharge burnup. For the higher burnups currently under consideration, these exposures could more than double at the end of life. At the same time, utilities and fuel vendors are demanding increasingly higher cladding performance with a target of zero failures.

The main degradation mechanisms suffered by cladding are uniform and localized waterside corrosion and hydriding, radiation embrittlement, radiation creep and growth and degradation of mechanical properties by a combination of radiation damage and hydriding. These property changes are connected to in-reactor microstructural and microchemical changes, including formation of dislocation loops, second phase particle amorphization and dissolution and a higher concentration of alloying elements in the matrix. Furthermore, the as-fabricated cladding when inserted in the reactor has had its properties optimized by a combination of heat treatments, composition and cold-working.

Most of the research that has optimized the composition and microstructure of Zr alloys in the past decades has been empirical in nature, and relied on extensive testing and development. In order to understand the changes and microstructure evolution and be able to predict cladding behavior in a more mechanistic way, it is necessary to better characterize the microstructure and microchemistry of these alloys at a sub-micron nanoscale and at concentrations at the trace element level. Much useful work has been done using Transmission electron microscopy (TEM), and now this can be complemented using the APS.

A collaborative research program between Penn State and Argonne National Laboratory has used the Advanced Photon Source (APS) at Argonne for a systematic study of alloying elements and second-phase particles in Zr alloys and their oxides. We will exemplify our research program by showing how we can answer three questions:

1. What is the alloying element content in the matrix of various Zr alloys?
2. What is the volume fraction of the second phase precipitates?
3. Are variations in oxide structure responsible for the different corrosion behavior of different Zr alloys? If so, what are critical oxide characteristics?

We will show how we are attempting to answer these questions by using the 2-ID-D/E and 2BM beamlines at APS, and how the information we gather relates to the modeling of degradation processes and to other experimental information from TEM and other sources.

Dr. Paul Evans (Lucent Technologies)

Future Directions in Materials Physics with an X-ray Microprobe

A variety of new developments in materials science and condensed matter physics at the nanometer scale await access to a dedicated focused x-ray facility. Hard x-ray optics including zone plates and focusing mirrors produce a submicron spot which can be used to make local quantitative measurements of strain, magnetization, and composition. Recent studies of strain in semiconductor electronic and optoelectronic devices, characterization of reaction products in combinatorial chemistry, and magnetization in rare earths suggest directions for future work. Potential long-term research directions are the physics of single domains in ferroelectric or magnetic materials, strain in self-organized and patterned electronic materials, and the development of innovative x-ray scattering techniques. It may even be possible to study in-situ the growth processes biological minerals.

Dr. Gene Ice (ORNL)

Frontiers of nanodiffraction with synchrotron radiation

Intense x-ray microbeams from 3rd generation synchrotron sources provide new opportunities for the study of nanoscale crystalline materials. As the x-ray probe size decreases, the x-ray diffraction pattern transitions from a standard powder pattern to diffraction from a discrete number of crystals. For nanomaterials the beam probe size required to enter this new regime is very small (<100 nm). For example, a 100nm-D x-ray beam will intercept ~90 10nm-D crystals close packed in a single layer. At most ~ 10 diffraction patterns can be untangled from the overlapping patterns so dispersion of the crystals, smaller beams or larger crystals is essential. For highly perfect nanocrystals, correlation lengths contain information about the morphology, and relaxed crystalline lattice. Diffraction anomalous fine structure (DAFS) can be used to determine further details about site occupation, oxidation state, and crystalline structure. Polychromatic x-ray microbeams with nondispersive focusing optics are especially well suited to this kind of study because the sample does not need to rotate. For greatest signal-to-noise and for a full reciprocal space map of the diffraction from each nanocrystal, the energy of the incident x-ray beam can be scanned while the beam is focused with nondispersive optics.

Dr. Robert M. Suter (Carnegie-Mellon University)

Microstructure of Polycrystalline Materials and Fluid Wetting of Solid Surfaces

I will give brief summaries of two research areas in which micro- to nano- sized x-ray beams will supply needed information to well known and technologically important problems.

I. The nature of the microstructure of polycrystalline materials determines many macroscopic properties. Grain boundaries between crystallites can be weak links where cracking, chemical corrosion, and/or electromigration damage occur. On the other hand, some grain boundaries are robust against such degradation. To generate optimized materials, we need to understand the mechanisms of microstructure evolution so that optimized networks can be produced. There has been no probe that could map three dimensional grain boundary networks and yield knowledge of the misorientation of adjacent grains until the current development of the Three Dimensional X-ray Diffraction Microscope (3DXDM) at ESRF.¹ This system uses high energy (40 - 80 keV) photons focused to ~1 micron to image diffraction from and map the location of individual grains in bulk (mm - cm thick) materials. We are able to watch microstructure evolve in real-time. At present however, we are restricted by both x-ray beam size and detector resolution to the study of large grained materials. Ideas for improving spatial resolution using smaller beams will be presented.

II. When a fluid contacts a solid surface, molecules close to the three phase contact line are uniquely affected by their proximity to all three phases. The microscopic interactions and resultant structures of these molecules determine the macroscopically observed static and dynamic contact angles. Molecular re-arrangements at a moving contact line determine the nature and extent of the wetting process. Except for cases of nearly complete wetting, traditional optical techniques for studying near-contact line behavior are limited by experimental geometry to long working distances resulting in resolutions ~10 microns. For common fluids, this is too coarse to observe the microscopically dominated region. We² are developing small beam x-ray probes that should improve spatial resolution by more than an order of magnitude. We use reflectivity measurements in the region of microscopic thin films which exist ahead of the contact line and one of several "x-ray profiling" measurements of the liquid-vapor interface shape in the region where the fluid becomes too thick to resolve by reflectivity. In many cases, we expect that micron sized beams will also be too large to resolve the fundamental interactions critical to wetting. Hence, there is an immediate need for nano-scale beams.

¹ Beamline ID-11 was developed by H.F. Poulsen and co-workers at Risoe National Laboratory, Denmark. The CMU group collaborates on data analysis software development and applications. CMU work is supported primarily by the MRSEC program of the NSF under Award Number DMR-0079996.

² This work is done in collaboration with S. Garoff and P. Wynblatt and is supported primarily by the NSF under Award Number DMR-9802290

Prof. Michael J. Bedzyk (Northwestern University)
X-ray Standing Wave and Scattering Studies of Nanostructures

We will discuss two prospective types of experiments:

- 1) How one might apply micro-beam x-ray standing waves to observe ferroelectric thin film domain growth during polarity switching.
- 2) How one can grow a 2D periodic epitaxial nanodot array and use the diffraction grating effect [1] from the entire array to enhance the sensitivity for measuring the form factor for a single nanodot and the strain in the surrounding substrate.

[1] Q. Shen and S. Kycia, Phys. Rev. B 55, 15791-15797 (1997).

Dr. Wojtek Dmowski (University of Pennsylvania)
Local Atomic Order Investigated by the Pair Distribution Function Obtained from X-ray and Neutron Scattering

The structure determination is one of the most important tasks in the materials studies. If the arrangement of atoms is highly regular as in many crystalline solids, standard crystallographic methods, such as the Rietveld analysis of the diffraction (Bragg) peaks, would allow the determination of the symmetry, unit cell and atomic positions. However, frequently materials of technological or scientific interest are not so perfect, and could be significantly disordered or inhomogeneous. In fact often these imperfections or inhomogeneities are crucial for the material properties of interest. Since the crystallographic methods focus only on the Bragg peaks in the diffraction patterns, one tends to classify materials simply crystalline when they exhibit Bragg peaks and glassy when a strongly diffuse pattern is observed. However, many complex materials are between these two extremes, and can have extensive internal disorder even when sharp Bragg peaks are observed. We suggest that the use of atomic pair distribution function (PDF) analysis greatly helps to elucidate the structure of complex materials. The PDF is obtained from the diffraction pattern by the direct Fourier-transformation of the total scattering including both the Bragg peaks and diffuse scattering intensity. It gives direct information, albeit one dimensional, about the distribution of the interatomic distances. We will illustrate the use of the PDF with two interesting results: the studies of relaxor ferroelectric Pb-based perovskite oxides and nanoparticle mixed electron-proton conductors, hydrous RuO₂. In the case of the ferroelectric relaxor, lead-scandium-tantalate (PST), the diffraction pattern, processed by a standard analysis, suggest a simple ideal perovskite structure. In reality, however, Pb atoms are significantly displaced from the high symmetry positions with medium-range correlations. Diffraction patterns from hydrous RuO₂ suggest strongly disordered, amorphous structure. However, the PDF analysis indicates that even for a high water content RuO₂-2.3H₂O there is strong rutile-

like short range atomic order at distances below 4 Å. The range of order increases with decreasing water content, and the structure approaches that of pure RuO₂. The use of PDF was instrumental in both cases to shed light on the real structure and to elucidate puzzling properties of these important materials.

Dr. Esen Alp (Argonne National Laboratory)

What can High Energy Resolution X-ray Scattering Offer for Nanoscale Science

The experimental study of dynamical behavior of condensed matter in nanoscale confined environments proves to be difficult due to length, energy, and momentum scales involved. The scientific breadth of the field is very wide, including fundamental understanding of friction, transport properties of fluids in porous media like zeolites, phonon propagation and folding in multilayers, dynamics of self-assembled liquid crystals, and glass transition. While it is possible to learn about many characteristics of confined systems in terms of atomic structure, and continuum properties, the dynamical properties at length scales comparable to intermolecular distances, and comparable to confined dimension of the geometry remains elusive. In this regard, inelastic x-ray scattering, and inelastic nuclear resonant scattering with very high energy resolution offers some unique possibility to probe these internal excitations "in-situ" in such a way that the perturbation due to measuring probe is negligible. The recent literature is very rich in terms of different types of phenomena in diverse fields such as biology, medicine, chemistry, physics, oceanography, geophysics, and chemical engineering.

Magnetism in thin films, islands, dots, and the interfaces can also be studied using nuclear resonant scattering, if they contain materials like Fe, Eu, and Dy. It is possible to measure, magnetic moments induced on these atoms, through measurement of nuclear hyperfine magnetic interaction strengths.

The state-of-art in inelastic scattering is the use of visible light, neutrons and x-rays, electrons, and helium atoms as probes. In this slew of techniques, x-rays occupy a special place in terms momentum-energy transfer range, penetration, and ability to probe buried interfaces. The current instruments with 2 meV resolution, and limited flux can be enhanced by an order of magnitude with improvements at the source, and monochromatization, and the energy analysis components, to make it suitable for study of nano-scale materials, and impact of reduced dimensions. Sector 3 of SRI-CAT presents good opportunity to test some of these ideas quickly, and implement the changes for an enhanced performance.

Dr. Jan Hessler (Argonne National Laboratory)

New Detectors for Time Resolved SAXS Measurements

Small-angle X-ray scattering (SAXS) measurements probe the structure of nanoscale materials, length scales below 30 nm. The current detector used for SAXS measurements is a mosaic CCD detector with nine CCDs. Although exposures below one second can be obtained, the time required to transfer information from the detector to a computer is at least 1.2 seconds. We have designed a new detector, which performs the azimuthal

averaging normally done with software, that will allow us to perform SAXS measurements with a temporal resolution below 3.6 microseconds. Therefore, *in situ* measurements of fabrication processes can be performed with the temporal resolution needed to identify the fundamental chemistry and physics of the process. In addition, a next generation detector, which is based on a micro-machining process, will be described. Theoretically this detector can have a temporal resolution as low as 10 nanoseconds. Examples of how these detectors can be used to study the fabrication of nanoscale materials will be described.

Prof. Chris Jacobsen (State University of New York at Stony Brook)

Soft Matter Nanoscience: Soft X-ray Focusing and Spectromicroscopy on Biological and Environmental Specimens

Soft x-ray spectromicroscopy is used to image micrometer-sized, wet specimens at 30-50 nm spatial resolution and 0.1-1.0 eV energy resolution. This capability is due in part to zone plate optics fabricated in collaboration with Lucent Technologies Bell Labs, and recent developments in this area are described. Studies of nanoscale heterogeneities in environmental, biological, and astrobiological specimens will be described. A brief mention will also be made of nanoscience plans under development at Brookhaven National Laboratory.

Dr. Gayle Woloschak (Argonne National Laboratory)

NANO-TITANS: Interactions of TiO₂ Nanoparticles Bound to Oligonucleotides with Nucleic Acids and Introduction into Mammalian Cells

Experiments were designed to test the possibility of using TiO₂ nanoparticles-biopolymer complexes as new vehicles for genetic engineering and gene therapy. Akin to nano-robots, complexes of TiO₂ nanoparticles with biopolymers may be used to remodel target DNA *in vitro* or *in vivo* through the use of the photoelectrical properties of TiO₂ and the electrical and biological properties of the attached biopolymers. We demonstrate that 43 nm TiO₂ nanoparticles with attached DNA oligonucleotides, developed by Rajh *et al.* (ibid), are able to penetrate cellular and nuclear membranes, and to be retained in the cell. Engagement in PCR reaction shows that the oligonucleotides attached to TiO₂ anneal/hybridize to the target DNA and participate in enzymatic reaction. As demonstrated by Rajh *et al.* (ibid) upon illumination positive holes (h⁺) and electrons (e⁻) are created in TiO₂ nanoparticles as a result of charge separation, and the holes (h⁺) transferred onto the attached oligonucleotide. Here we describe that illumination of the completed PCR products containing the TiO₂ nanoparticles causes DNA strand breaks within short distance from the attached TiO₂ nanoparticles, presumably due to the accumulation of holes (h⁺) in guanidine bases.

Dr. Mike Fitzsimmons (Los Alamos National Laboratory)

Asymmetric Magnetization Reversal in Exchange Bias Systems

Polarized neutron reflectometry measured the in-plane projection of the net-magnetization vector of polycrystalline Fe films exchanged-coupled to FeF₂ antiferromagnetic (AF) films of controlled crystalline quality. These measurements, which included ones of single crystalline, twinned and textured polycrystalline (110) FeF₂ films, demonstrate that asymmetry in the magnetization reversal process on either side of the ferromagnetic (F) hysteresis loop is an important factor determining exchange bias—the shift of the hysteresis loop from zero applied field. For the AF single crystal sample, we observed perpendicular exchange coupling across the F-AF interface which is manifested by symmetric production of neutron spin-flip scattering on either side of the hysteresis loop at coercivity. Perpendicular exchange coupling was observed regardless of cooling field orientation even though exchange bias (though small) was clearly affected by the cooling field orientation, thus, perpendicular exchange coupling is not a sufficient condition for exchange bias. For samples with a twinned AF, an asymmetry in the spin flip scattering on either side of the hysteresis loop, and consequently in the magnetization reversal process, was observed. The origin of the asymmetry is shown to be frustration of the perpendicular exchange coupling, which enhances exchange bias and leads to 45° exchange coupling across the F-AF interface.

*Work supported by the U.S. Department of Energy, BES-DMS under Contract No. W-7405-Eng-36, Grant No. DE-FG03-87ER-45332 and funds from the University of California Collaborative University and Laboratory Assisted Research.

†Work in collaboration with A. Hoffmann, P. Yashar, J. Groves, R. Springer, P. Arendt (LANL), C. Leighton, K. Liu, Ivan K. Schuller (UCSD), J. Nogués (UAB), C.F. Majkrzak, J. Dura (NIST), H. Fritzsche (HMI).

Dr. John Freeland (Argonne National Laboratory)

Characterizing magnetic nanostructures with polarized x-rays

X-rays are a powerful tool for element specific analysis of magnetic order. Polarization dependent spectroscopy enables characterization of spin and orbital contributions to the net magnetization as well as being able to perform element specific monitoring of changes with applied magnetic field. In sector 4 of the Advanced Photon Source, we are developing a polarization dependent facility coupling microscopy and spectroscopy to probe the influence of dimensionality on magnetic order. Future plans for both science and instrumentation will be discussed and illustrated with results of ongoing research. Work supported by the U.S. Dept. of Energy, Office of Science, contract no. W-31-109-ENG-38.

Dr. George Srajer (Argonne National Laboratory)

Magnetic Imaging with a Circularly Polarized Microprobe

We report on the development of a circularly polarized x-ray microprobe in the intermediate energy range from 5 to 10 keV. By combining microfocusing capabilities

with magnetic x-ray scattering techniques, this probe extends x-ray imaging techniques to the measurement of the micron-scale magnetic distribution within the sample. Previous work in this field has been performed in the soft x-ray regime. This probe, on the other hand, is designed for hard x-rays, which allows for the ability to probe buried magnetic structures. The properties of the microprobe were characterized, and the technique was applied to the two-dimensional mapping of magnetic domains in HoFe_2 and SmCo/Fe

The work at the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Office of Energy Research, under contract W-31-109-ENG-38 at Argonne National Laboratory.

Dr. Jeff B. Kortright (Lawrence Berkeley National Laboratory)

Soft X-ray Techniques to Study Magnetic Nanostructures

By extending Faraday and Kerr magneto-optical techniques from the near-visible spectral ranges, and resonant magnetic scattering from the hard x-ray spectral range, into the soft x-ray spectral range we gain unprecedented sensitivity to magnetism in materials containing the $3d$ transition elements by working near their $2p$ core resonances.¹ Emerging techniques using this resonant magneto-optical sensitivity provide numerous opportunities to study the structure of magnetic nanostructures and magnetism at nanometer length scales. Element-resolved magnetic information naturally results from resonant Faraday and Kerr spectroscopy techniques measuring both phase and intensity. While these spectroscopies yield information laterally averaged over illuminated volumes, they provide improved depth resolution (compared to near-visible MOKE) to enable studies of the depth variation magnetization near buried interfaces. Spatial resolution down of order 1-10 nm is obtained from scattering (in reciprocal space) and imaging (in real space). Examples using these different techniques will be given, with emphasis on their complementary nature.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science, of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

1. A recent review of opportunities to study magnetism using soft x-ray is in: J. B. Kortright, D. D. Awschalom, J. Stohr, S. D. Bader, Y. U. Idzerda, S. S. P. Parkin, I. K. Schuller, and H.-C. Siegmann, *JMMM* **207**, 7-44 (1999).