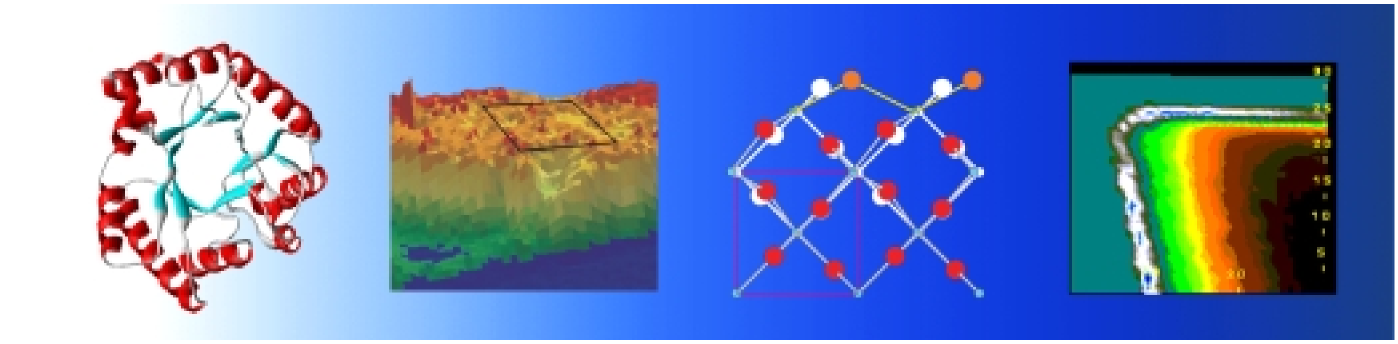
Workshop 1: Nanoscale Science Using Synchrotron Techniques

Brian Stephenson and John Carlisle, organizers

Tuesday, October 9, 2001
8:30 am–Noon & 1:30–5:00 pm



Nanoscience is an emerging, multidisciplinary field involving the study of materials having novel properties and functionality due to confinement and proximity effects at the 1–100 nm length scale. To fabricate nanoscale structures, both “top-down” (e.g., lithographic) and “bottom-up” (e.g., molecular self assembly) approaches are being pursued, often in combination, using hybrids of various types of materials. Nanoscience draws from fundamental synthesis and characterization tools taken from all the traditional fields of science: chemistry, physics, materials science, and molecular biology. This workshop will focus on current status and future prospects for synchrotron-based nanoscale characterization. Presentations will highlight current scientific results relevant to this rapidly evolving area, novel technical features of beamlines and experiments, and new directions in nanoscience at APS.

8:00–8:25 am	**Registration and Reception**
8:25–8:30 am	**Welcome** Brian Stephenson and John A. Carlisle, *Argonne National Laboratory*
8:30–9:00 am	**Quantum Wells and Wires at the Atomic Limit** Franz J. Himpsel, *University of Wisonsin-Madison*
9:00–9:30 am	**Nanocluster Properties Characterized Using Soft X-ray Spectroscopies** Louis J. Terminello, *Lawrence Livermore National Laboratory*
9:30–10:00 am	**Surface Restructuring of TiO_2 Nanoparticles Revealed by X-Ray Spectroscopies** Tijana Rajh, *Argonne National Laboratory*
10:00–10:30 am	**Refreshments**
10:30–11:00 am	**NEXAFS Scanning Transmission Microscopy: A Nanoscale Characterization Tool for Polymeric Materials** Harald Ade, *North Carolina State University*
11:00–11:30 am	**Characterization of Nanostructures by Small-angle and Wide-angle High-energy X-ray Scattering** Randall Winans, *Argonne National Laboratory*
11:30 am–1:30 pm	**Lunch**
1:30–2:00 pm	**The Center for Nanoscale Materials** Murray Gibson, *Argonne National Laboratory*

2:00–2:30 pm	**Plans for a Hard X-ray Nanoprobe Beamline at the APS** Jorg Maser, *Argonne National Laboratory*
2:30–3:00 pm	**Single Domain Studies with X-ray Microscopy** Eric Isaacs, *Bell Laboratories, Lucent Technologies*
3:00–3:30 pm	**Refreshments**
3:30–4:00 pm	**The X-ray Microscopy and Micro-analysis Facility at the ESRF** Jean Susini, *European Synchrotron Radiation Facility*
4:00–4:30 pm	**Magnetic Domains Imaging at the APS** George Srajer, *Argonne National Laboratory*

Quantum Wells and Wires at the Atomic Limit

Franz J. Himpsel, *University of Wisconsin Madison, Madison, WI 53706 USA*

Two-dimensional quantum wells and one-dimensional quantum wires can now be engineered with atomic precision. They provide a testing ground for the idea of tailored solids, where the electronic properties are controlled by confining electrons to regions comparable to their wavelength. This talk will review the growth of atomically precise silver layers [1] with magical thicknesses [2] and the self-assembly of atomic wires on silicon [2]. Unusual electronic states are found by angle-resolved photoemission, such as a band with variable dimensionality [3]. The hunt for even more exotic phenomena is on, such as the separation of an electron into two quasiparticles, one carrying its spin, the other its charge [4].

[1] J.J. Paggel *et. al*., *Science* **283**, 1709 (1999); F.J. Himpsel, *Science* **283**, 1655 (1999).
[2] D.-A. Luh *et. al*., *Science* **292**, 1131 (2001).
[3] R. Losio *et. al*., *Phys. Rev. Lett*. **85**, 808 (2000).
[4] R. Losio *et. al*., *Phys. Rev. Lett*. **86**, 4632 (2001).

Nanocluster Properties Characterized Using Soft X-ray Spectroscopies*

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The scientific world is embracing all types of nanoscience and technology through the rapidly advancing work seen in the scientific community. Central to this work is the control of properties for novel nanostructured materials, and how to incorporate them into useful devices. At LLNL, we have used third-generation synchrotron radiation from the Advanced Light Source (Berkeley, CA) to perform x-ray absorption spectroscopy (XAS), photoelectron spectroscopy (PES), and soft x-ray fluorescence (SXF) experiments on a variety of nanostructured materials in order to better understand the properties of these novel compounds. The reduced dimensional materials characterized include diamond, Si, Ge, and MoS_2 nanoclusters ranging is size from 1–12 nm. In each case we have exploited the element selectivity of the soft x-ray methods to probe the electronic structure, bonding, and morphology of these materials as a function of particle size. In particular, we use soft x-ray probes to determine band-shift and surface effects in our nanocluster samples. For many of these material systems, knowledge of band gap widening with quantum confinement, band alignment, and surface effects is critical to rational design and utilization of these novel materials in diverse applications.

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Surface Restructuring of TiO_2 Nanoparticles Revealed by X-Ray Spectroscopies

T. Rajh, L.X. Chen, T. Liu, D.M. Tiede, and M.C. Thurnauer, *Chemistry Division, Argonne National Laboratory, Argonne IL 60439 USA*

Ligand-induced surface reconstruction was found to be an efficient route for linking biomolecules to metal oxide nanoparticles. Under-coordinated defect sites appearing in nanocrystalline TiO_2 are the sources of novel enhanced and selective reactivity of the nanoparticle toward bidentate ligand binding. The stability of the complex of surface defects with enediol ligands is enhanced due to ligand induced reconstruction of the nanoparticle surface. The unique bidentate binding results in new hybrid properties. As a result, in these CT nanocrystallites the onset of absorption is shifted to the red, as compared to unmodified nanocrystallites. Similar chemistries were found for nanocrystalline Fe_2O_3 and ZrO_2. The ligating reagents were explored as conductive leads to a variety of biomolecules. Parameters enhancing light induced electron transfer between metal oxide nanoparticles and targeted external electron acceptors and donors are identified. This approach can result in a generally applicable chemical technology for photoactivation and charge transfer at the biomolecule-metal oxide interface.

NEXAFS Scanning Transmission Microscopy: A Nanoscale Characterization Tool for Polymeric Materials

H. Ade, *Dept. of Physics, North Carolina State University, Raleigh, NC 27695 USA*

Since the first demonstration of transmission NEXAFS microscopy in 1992 [1], the technique has evolved into a quantitative analysis tool with a few percent accuracy at a spatial resolution of less than 100 nm [2, 3]. The combination of high spatial resolution, low beam damage [4], and quantitative compositional sensitivity is unique, and makes NEXAFS microscopy an excellent complement to high “chemical content” microscopies, such as NMR, IR, and Raman microscopy, and high “spatial resolution” microscopes, such as various electron microscopes. NEXAFS spectra are also dependent on the orientation of bonds, and the resulting linear dichroism can be used to characterize the orientation of molecules in bulk materials [5, 6]. We present several applications involving polymeric systems as examples. We will also review two recent instrument developments at the ALS. One of these is a bending magnet scanning transmission x-ray microscope optimized for applications of carbonaceous materials. After a short commissioning period, excellent performance has already been achieved. In the near future, the spatial resolution should improve to <30 nm making NEXAFS transmission microscope a true nano-characterization tool.

[1] H. Ade *et. al*., *Science* **258**, 972 (1992).
[2] S.G. Urquhart *et. al*., *J. Electron Spectrosc. Relat. Phenom*. **100**, 119 (1999).

[3] H. Ade and S. Urquhart, in *Chemical Applications of Synchrotron Radiation*, T. K. Sham, Eds., (World Scientific Publishing, 2001).
[4] E.G. Rightor *et. al*., *J. Phys. Chem. B* **101**, 1950 (1997).
[5] H. Ade and B. Hsiao, *Science* **262**, 1427 (1993).
[6] A.P. Smith and H. Ade, *Appl. Phys. Lett*. **69**, 3833 (1996).

Characterization of Nanostructures by Small-angle and Wide-angle High-energy X-ray Scattering*

Randall E. Winans, *Chemistry Division and BESSRC CAT, Argonne National Laboratory, Argonne, IL 60439 USA*

Small-angle x-ray scattering (SAXS) is able to provide size, shape, density, and surface properties on the length scales found in nanostructures. This approach is especially useful for in situ observations of structural transformations in disordered systems. An example is the formation of nanocarbons in flames. We have been able to observe for the first time nanocarbons as small as 0.8 nm which have not been observed *in situ* by other methods such as with lasers. It should be possible to monitor the growth of nanotubes produced catalytically in flames. It is difficult to obtain short-range order information on nanostructures. However, high-energy (115 keV) wide-angle scattering using pair distribution function analysis can be used to describe the environment of individual atoms in nanostructures. Initial studies have been done on clusters in solution and nanocarbons.

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The Center for Nanoscale Materials

J.M. Gibson, *Division Director, Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 USA*

Argonne's strategic plan is to establish the Center for Nanoscale Materials, which will offer unique facilities for synthesizing and characterizing nanostructures. Expected facilities include electron-beam lithography, advanced microscopies (including electrons, proximal probes and x-rays), and molecular self-assembly. The Center will bring the unique capabilities of APS and Argonne to bear on nanoscience research. The Center will be open to usage by outside researchers, in fact, it is not too late for outsiders to influence the direction of development of the Center. The State of Illinois is contributing to the building of the Center. The Argonne Nanotechnology Research Institute, a State-of-Illinois funded entity, will help to make the facilities available to State institutions.

Plans for a Hard X-ray Nanoprobe Beamline at the APS

Jörg Maser, *Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439 USA*

With the advent of high-energy, third-generation synchrotrons, hard x-ray microprobes with sub-micron resolution have become feasible. The first generation of these systems have proven to be powerful probes of the properties of hard and soft matter using techniques such as x-ray fluorescence mappingand spectroscopy, diffraction contrast imaging, and transmission imaging.

We plan to develop a next-generation hard x-ray probe with a spatial resolution of 30 nm. The system will span an energy range of 3–30 keV. It will combine a scanning probe mode with a full-field transmission mode. The scanning probe mode will utilize secondary signals such as fluorescence photons and scattered radiation for elemental mapping, chemical state mapping and diffraction contrast imaging. The full-field transmission mode will utilize absorption and phase contrast imaging for applications such as high-resolution imaging and tomography.

We will outline the first plans for the beamline and the concept for the probe instrument.

Single Domain Studies with X-ray Microscopy

Eric D. Isaacs, *Semiconductor Physics Research, Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974 USA*

The interplay between macroscopically observable phenomena and the configuration of domains and domain walls, both magnetic and ferroelectric, is becoming increasingly important as density requirements in many technologies drive device feature sizes towards those of individual domains. Through synchrotron based x-ray microscopy techniques we are making important first steps towards understanding the relationship of microscopic domains to the bulk properties. We will describe several examples including how domain walls in Cr seed the low-temperature spin-density wave state and how strain gradients near grain boundaries account for the unusual special and temperature dependence of the magnetically ordered state in CMR films.

The X-ray Microscopy and Micro-analysis Facility at the ESRF

Jean Susini, *European Synchrotron Radiation Facility, Grenoble Cedex, France*

X-ray microscopy (XRM) techniques are emerging as powerful and complementary tools for sub-micron investigations. Soft XRM offers traditionally the possibility to form direct images of thick hydrated material in near-native environment, at a spatial resolution well beyond that achievable with visible light microscopy. Natural contrast is available in the soft x-ray region, in the so-called “water-window”, due to the presence of absorption edges of the major constituents (C, N, O). Recent advances in manufacturing techniques have enlarged the accessible energy range of micro-focusing optics to higher energies and offer new applications in a broad range of disciplines. This x-ray microscopy for energies higher than 1 keV exhibits complementary attributes such as:
i) The access to K-absorption edges and fluorescence emission lines of medium-light elements and L,M - edges of heavy materials allows micro-spectroscopy (e.g., XANES), chemical mapping, trauce element mapping and specimen labelling with high spatial resolution
ii) The higher penetration depth compared to soft x-rays allows imaging of thick samples ($10 < t(\mu m) < 100$), in particular in their natural environment.
iii) Large focal lengths (> 10 mm) and depths of focus (> 50 μm) give suitable conditions for specific sample environments and x-ray tomography.
iv) The control of the linear or circular polarisation at K-edges of transition metals, L-edges of rare earths and M-edges of actinides opens new windows of applications in x-ray magnetic circular dichroism and magnetic diffraction within the micron scale.

This presentation will be biased towards sub-micron microscopy developed on the x-ray microscopy beamlines, ID21, ID22, and ID18F, at the ESRF. Following a brief account on the characteristics of these beamlines, strengths and weaknesses of x-ray microscopy and spectro-microscopy techniques in the 1–20 keV range will be discussed and illustrated by examples of applications. The main technical developments, involving new focussing lenses or novel phase contrast geometry, will be presented.

Magnetic Domains Imaging at the APS

George Srajer, *Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439 USA*

Imaging of magnetic domains with a focused beam will be presented. The experiment was performed on a SmCo/Fe sample, which belongs to an important class of nanocomposite materials called “spring magnets.” For the first time, information on the size, orientation, and distribution of Sm moments were revealed. The application of magnetic scattering techniques to the study of magnetic nanoarrays will be discussed as well.