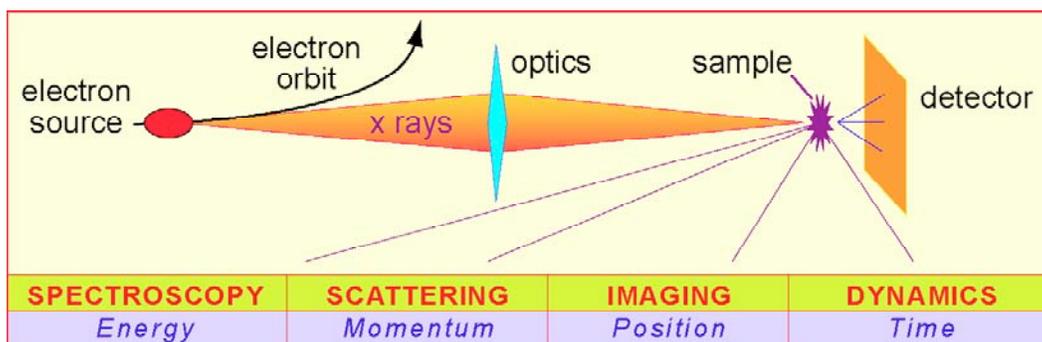


# EXPERIMENTAL TECHNIQUES AT LIGHT-SOURCE BEAMLINES

## INTRODUCTION

The unique properties of synchrotron radiation are its continuous spectrum, high flux and brightness, and high coherence, which make it an indispensable tool in the exploration of matter. The wavelengths of the emitted photons span a range of dimensions from the atomic level to biological cells, thereby providing incisive probes for advanced research in materials science, physical and chemical sciences, metrology, geosciences, environmental sciences, biosciences, medical sciences, and pharmaceutical sciences. The features of synchrotron radiation are especially well matched to the needs of nanoscience.

This breadth of problems requires an extensive suite of probes. The basic components of a beamline, however, share general similarities as shown in the schematic diagram below.



The fundamental parameters that we use to perceive the physical world (energy, momentum, position, and time) correspond to three broad categories of synchrotron experimental measurement techniques: spectroscopy, scattering, and imaging. By exploiting the short pulse lengths of synchrotron radiation, each technique can be performed in a timing fashion.

**SPECTROSCOPY** techniques are used to study the energies of particles that are emitted or absorbed by samples that are exposed to the light-source beam and are commonly used to determine the characteristics of chemical bonding and electron motion.

**SCATTERING** or diffraction techniques make use of the patterns of light produced when x-rays are deflected by the closely spaced lattice of atoms in solids and are commonly used to determine the structures of crystals and large molecules such as proteins.

**IMAGING** techniques use the light-source beam to obtain pictures with fine spatial resolution of the samples under study and are used in diverse research areas such as cell biology, lithography, infrared microscopy, radiology, and x-ray tomography.

<b>SPECTROSCOPY</b>
01 Low-Energy Spectroscopy
02 Soft X-Ray Spectroscopy
03 Hard X-Ray Spectroscopy
04 Optics/Calibration/Metrology

<b>SCATTERING</b>
05 Hard X-Ray Diffraction
06 Macromolecular Crystallography
07 Hard X-Ray Scattering
08 Soft X-Ray Scattering

<b>IMAGING</b>
09 Hard X-Ray Imaging
10 Soft X-Ray Imaging
11 Infrared Imaging
12 Lithography

The three broad categories may be subdivided into twelve basic techniques. The following pages offer a brief description of each technique and some examples of research performed using that technique.

## 01: LOW-ENERGY SPECTROSCOPY

**OTHER DESIGNATIONS:** Vacuum-ultraviolet (VUV) spectroscopy, photoelectron spectroscopy (PES), angle-resolved photoelectron spectroscopy (ARPES), photon-ion spectroscopy, infrared (IR) spectroscopy, terahertz (THz) spectroscopy, ultraviolet photoemission spectroscopy (UPS), cold-target recoil-ion momentum spectroscopy (COLTRIMS), photoelectron-photoion coincidence (PEPICO) spectroscopy, Fourier transform infrared (FTIR) spectroscopy.

**PURPOSE:** Probes that use the VUV region of the spectrum (10–100 eV) are very well matched to the elucidation of bonding in solids, surfaces, and molecules; to the investigation of electron–electron correlations in solids, atoms, and ions; and to the study of reaction pathways in chemical dynamics. At the lowest end of this energy range (below 1 eV) we have infrared, far-infrared, and terahertz spectroscopies, which are well matched to vibrational modes and other modes of excitation. Problems addressed include:

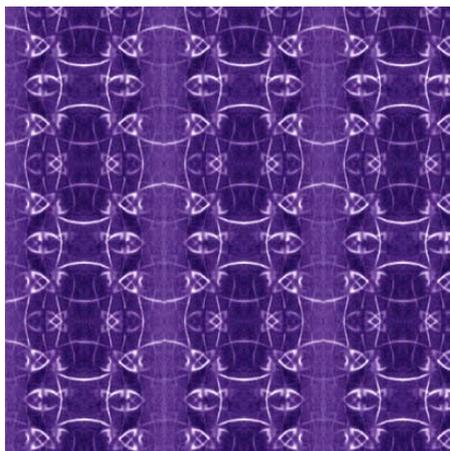
- Complex materials
- Surfaces, clusters
- Atomic and molecular physics, astrophysics
- Combustion, chemical dynamics
- Biological systems

**HOW THE TECHNIQUE WORKS:** VUV spectroscopy is not a single technique but a myriad of techniques. The sample of interest, either solid or gaseous, is illuminated with light and the various product particles (electrons, ions, or fluorescent photons) are detected and analyzed. In ARPES experiments, for example, the sample is a single crystal having a clean, well-characterized surface. The directions and energies of the emitted photoelectrons are measured. Analysis of this data yields incisive information on the way electrons move within the sample. In gas-phase experiments, the detected particles can be electrons, ions, molecules, or clusters. Auxiliary techniques include mass spectrometry, time-of-flight and coincidence detection.

**UNIQUENESS:** The universal demand in this area is for a high signal rate with very high resolving power. The high brightness and small spot size achievable with synchrotron radiation, particularly at third-generation sources, permits the design and operation of very advanced monochromators, spectrometers, and electron-energy analyzers.

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### *Electron Waves in the Fermi Sea*



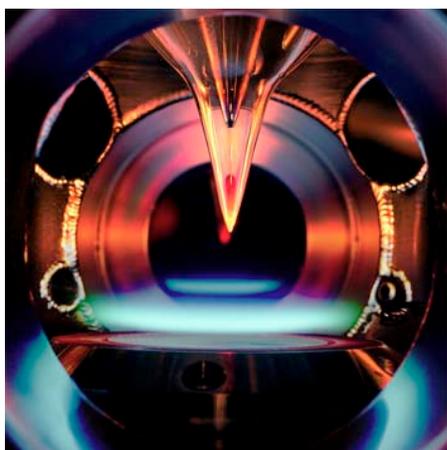
*The momentum distribution of electrons at the Fermi energy in a two-dimensional metal.*

E. Rotenberg, H. Koh, K. Rossnagel, H.W. Yeom, J. Schäfer, B. Krenzer, M.P. Rocha, and S.D. Kevan, "Indium  $\sqrt{7} \times \sqrt{3}$  on Si(111): A nearly free electron metal in two dimensions," *Phys. Rev. Lett.* **91**, 246404 (2003).

The electrons that conduct electricity in metals and semiconductors are important because they determine all of the major properties of conductors: not only those that are well understood but also those of the more exotic materials such as the high-temperature superconductors. Recent angle-resolved photoelectron spectroscopy (ARPES) experiments on a system comprising a monolayer of indium on a silicon substrate display the properties of a "nearly-free-electron" two-dimensional metal. If the electrons were perfectly free, those with energies near the Fermi energy would reside around a single perfect circle in momentum space. It is seen from the figure that the basic circle is repeated and folded back on itself in a highly convoluted way. This is because the electron waves are lapping against the background atomic lattice. From this kind of information one can deduce the way electrons move in solids.

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## Understanding the Fundamental Processes in Combustion



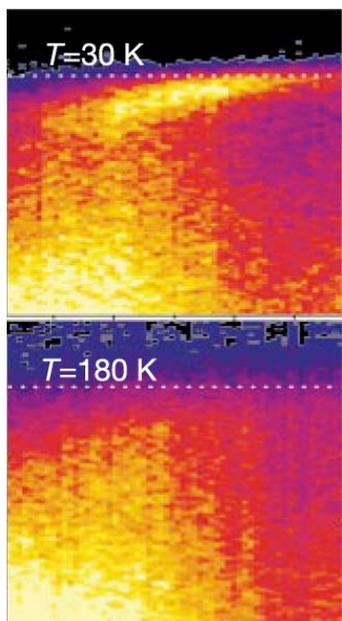
*Laminar-flow burner assembly.*

T.A. Cool, K. Nakajima, T.A. Mostefaoui, F. Qi, A. McIlroy, P.R. Westmoreland, M.E. Law, L. Poisson, D.S. Peterka, and M. Ahmed, "Selective detection of isomers with photoionization mass spectrometry for studies of hydrocarbon flames," *J. Chem. Phys.* **119**, 8356 (2003).

Combustion seems to be well understood in terms of average energy output, high-concentration intermediates, and major products. However, an understanding of flame chemistry is required for global models of combustion and also for controls relevant to emissions. Because of the complexity of the fluid dynamics of a "real" flame and the highly reactive nature of chemical states, many important rate constants have never been measured directly, nor have all the species included in theoretical models been directly observed. Scientists have developed a laminar-flow burner assembly that allows the real-time monitoring of the processes in an actual flame. It also permits the introduction of dopants so that the changes in chemistry that they produce can be studied. In these flames, the temperature and concentration profiles can be mapped to very high precision, a consequence of the laminar flow and the low-pressure conditions that make the flame reaction zone much larger than under atmospheric conditions. These benefits result in a machine with both increased sensitivity and near-universal selectivity. Combined with high-flux, continuous vacuum-ultraviolet (VUV) radiation, this machine offers the sensitivity and flexibility needed to study the complexities of combustion.

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## Dimensional Crossover in Layered Strongly Correlated Metals

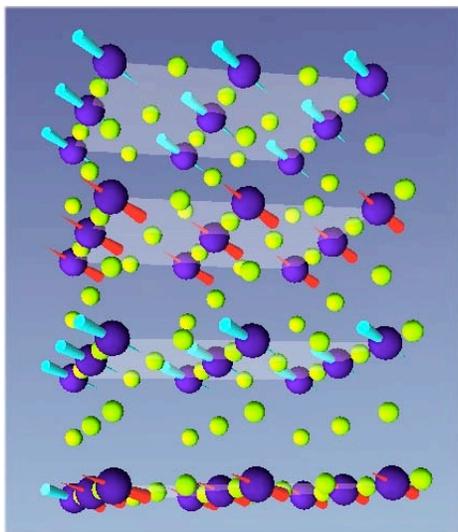


*Comparison ARPES spectra at two different temperatures.*

T. Valla, P.D. Johnson, Z. Yusof, B. Wells, Q. Li, S.M. Loureiro, R.J. Cava, M. Mikami, Y. Mori, M. Yoshimura, and T. Sasaki, "Coherence-incoherence and dimensional crossover in layered strongly correlated metals," *Nature (London)* **417**, 627 (2002).

Many new materials consist of one- or two-dimensional building blocks, loosely connected into a three-dimensional whole, resulting in highly anisotropic physical properties. Small interactions between the building blocks may induce a whole variety of unusual transitions. One of the most intriguing is a "dimensional crossover" in layered metals where, in the direction perpendicular to the layers, transport properties change from insulator-like at high temperatures to metallic-like at low temperatures, while remaining metallic over the whole temperature range in the direction parallel to the layers. Scientists examined two such layered metallic systems with angle-resolved photoemission spectroscopy (ARPES) and electronic transport measurements. They found a crossover in the number of effective dimensions — from two to three — with decreasing temperature. Within the conventional theories, this phenomenon is hard to understand. Recent photoemission experiments have shown that this change in effective dimensionality correlates with changes in the electronic spectra: sharp features associated with "quasiparticle-like excitations" only exist in the low-temperature three-dimensional-like phase, while they are absent in the effectively two-dimensional, high-temperature phase.

## Spin Interactions in Magnetic Oxides

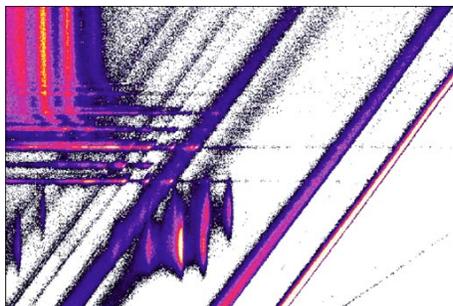


*Schematic representation of the spins (red and cyan cones) at the manganese sites of LaMnO<sub>3</sub>, showing their antiferromagnetic orientation.*

D. Talbayev, L. Mihaly, and J. Zhou, "Antiferromagnetic resonance in LaMnO<sub>3</sub> at low temperature," *Phys. Rev. Lett.* **93**, 017202 (2004).

The parent compound for many of the so-called "colossal magnetoresistance" (CMR) materials is lanthanum manganite (LaMnO<sub>3</sub>). These CMR materials have been instrumental in enabling recent advances in magnetic storage devices, yet their physical properties are yet to be fully understood. LaMnO<sub>3</sub> is an antiferromagnet, meaning that adjacent spins are aligned in opposite directions. When placed in the field of a large laboratory magnet, the spin of an electron can resonantly flip between two spin states. This resonance occurs at a characteristic frequency, usually in the microwave portion of the spectrum. If a stronger field is available, the resonance can be shifted into the terahertz or far-infrared spectral range. With this in mind, a group of researchers has developed an electron spin resonance (ESR) system using a high-field magnet and Fourier-transform infrared (FTIR) spectrometer system. With this system, spin resonance can be studied as a function of both magnetic field and frequency. The sharpness of the resonance is an indicator of how strongly the spin interacts with other excitations in the system. This new ESR system provides a method for measuring the resonance lifetime without sweeping the field (which can cause the resonance to change). Terahertz light from a synchrotron source provides the high power and brightness required to pass through the magnet's narrow windows. These studies of LaMnO<sub>3</sub> explain how the spins are "canted" relative to the crystal structure, and provide values for the interaction strength between different spins in the material.

## Electron Excitations At-A-Glance



*Two-dimensional spectrum of hydrogen chloride.*

E. Kukk, A. Wells, N. Berrah, B. Langer, J.D. Bozek, O. Nayandin, M. Alshehri, A. Farhat, and D. Cubaynes, "A ngle-resolved two-dimensional mapping of electron emission following Cl 2p excitations in the HCl molecule," *Phys. Rev. A* **57**, R1485 (1998).

Important questions in many areas of science and technology often hinge upon how atoms, molecules, and ions behave in a specific environment. For example, detailed knowledge of the electronic structure of solids must be built upon a thorough understanding of isolated atomic and molecular systems. With high-brightness synchrotron light and advanced data-acquisition technology, researchers have been able to record a complete, angle-resolved, two-dimensional picture of electron emission from a diatomic molecule, hydrogen chloride, over a comprehensive energy range. By plotting the energy of the incoming photons on the vertical axis and the kinetic energy of the ejected electrons on the horizontal axis, scientists can study the interplay between various excitations and photoemission processes as the photon energy is scanned across an ionization threshold. The locations and intensities of emission lines identify processes such as excitation to unoccupied molecular orbitals, excitation to Rydberg orbitals, and ionization into the continuum. Diagonal lines indicate the absorption of x-rays by electrons in outer (valence) molecular orbitals rather than deep inside the chlorine atom.

## 02: SOFT X-RAY SPECTROSCOPY

**OTHER DESIGNATIONS:** Soft x-ray absorption spectroscopy (XAS), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, soft x-ray emission spectroscopy (SXES), resonant inelastic x-ray scattering (RIXS), x-ray magnetic circular dichroism (XMCD), x-ray photoemission spectroscopy (XPS), Auger spectroscopy.

**PURPOSE:** Soft x-ray spectroscopies employ the excitation of electrons in relatively shallow core levels (100–2000 eV) to probe the electronic structure of various kinds of matter. Problems addressed include:

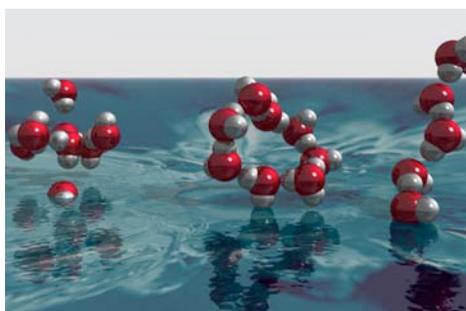
- Complex materials
- Magnetic materials
- Environmental science, wet samples at ambient pressure
- Catalysis

**HOW THE TECHNIQUE WORKS:** Soft x-ray spectroscopy is not a single technique but an array of techniques. The unifying feature is that some “property” of a material is measured as the x-ray (photon) energy is swept through a range of values. At the most basic level, one measures the absorption, transmission, or reflectivity of a sample as a function of photon energy. At a more sophisticated level, one can perform a “double” spectroscopy. In the case of “photon-in/electron-out,” one measures the energy spectrum of photoemitted electrons (XPS). In the case of “photon-in/photon-out,” one measures the spectrum of fluorescent or inelastically scattered photons (SXES, RIXS) and does this for a range of energies of the incident photon. Another dimension to the technique is circular polarization; certain chiral and magnetic systems respond differently to the left or right circularly polarized photons produced by special beamline insertion devices.

**UNIQUENESS:** Elemental specificity is the watchword for this kind of spectroscopy. Each element has its own set of core levels that occur at characteristic energies. The photon-energy tunability of synchrotron radiation is essential. Because of extremely low cross sections, the photon-in/photon-out techniques (SXES and RIXS) are viable only at brilliant synchrotron sources.

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### Rethinking the Structure of Water

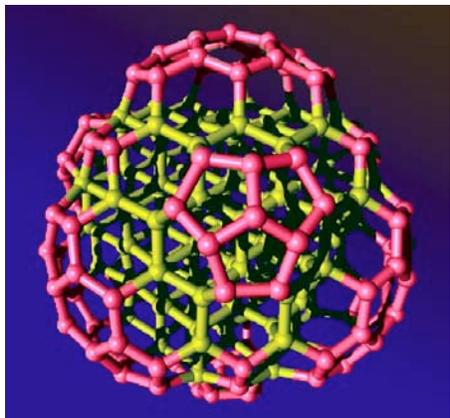


*Tetrahedral, ring, and chain structures in liquid water (courtesy of H. Ogasawara).*

Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odellius, H. Ogasawara, L.Å. Näslund, T.K. Hirsch, L. Ojamäe, P. Glatzel, L.G.M. Pettersson, and A. Nilsson, “The structure of the first coordination shell in liquid water,” *Science* **304**, 995 (2004).

Water is the key to our existence on this planet and it is involved in nearly all biological, geological, and chemical processes. Knowledge about how its molecules bond with each other is essential for understanding its unusual chemical and physical properties. In its condensed phase (i.e., ice), each water molecule bonds loosely to four others in a tetrahedral arrangement. For 20 years, it has been commonly accepted that liquid water also forms a semi-tetrahedral structure. Previous studies, relying largely on neutron and x-ray diffraction data, could not provide a unique experimental determination of local molecular arrangements. A different approach, using soft x-ray absorption spectroscopy (XAS), probes how chemical bonding perturbs the local valence electronic structure. From the data obtained, the researchers concluded that liquid water consists mainly of structures with two strong hydrogen bonds, in contrast to the four bonds found in the tetrahedral structure of ice. This new result resurrects models that were previously discarded, such as the possibility that water molecules form chains or closed rings. Eventually, the outcome could be a better understanding of the chemistry of the cell — notoriously hard to imitate using different liquids — and perhaps a clearer answer to why water is essential for life.

## Nanodiamonds Show Buckyball Surfaces

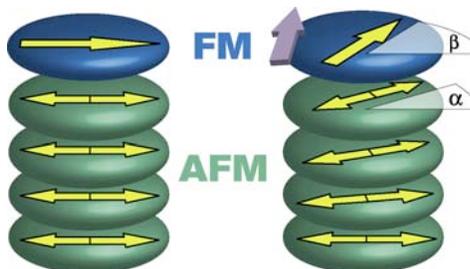


Ball-and-stick representation of bucky diamond cluster, showing diamond core (yellow) and a fullerene-like reconstructed surface (red).

J.-Y. Raty, G. Galli, C. Bostedt, T.W. van Buuren, and L.J. Terminello, "Quantum confinement and fullerene-like surface reconstructions in nanodiamonds," *Phys. Rev. Lett.* **90**, 037401 (2003).

Scientists have found that diamonds made of up to a few hundred carbon atoms ("nanodiamonds") do not exhibit the smooth, faceted surfaces commonly associated with crystals. Instead, at this scale, portions of the diamond's surface will spontaneously buckle into the curved, geodesic-dome structure found in buckyballs. The researchers came to this surprising conclusion after performing soft x-ray absorption and emission spectroscopy experiments on nanodiamonds synthesized in detonation waves from high explosives. Diamond, like silicon and germanium, is a semiconductor whose behavior depends on the size of its optical gap — the energy difference between its valence and conduction bands. Emission and absorption spectroscopy together reveal the optical gap in semiconductors, with emission revealing the valence band maximum and absorption revealing the conduction band minimum. The techniques also reflect the density of states around the band gap — a sensitive fingerprint of atomic bonding configurations. The nanodiamond absorption spectra showed features not observed in bulk diamond samples. Comparison to theoretical models suggests that the feature is the signature of the pentagonal and hexagonal bonding configurations found on buckyball-like surfaces. The discovery of this new family of carbon clusters, dubbed "bucky diamonds," may have implications for a wide range of areas, from astronomy, where diamonds are studied as a constituent of meteorites and interplanetary dust, to optoelectronics, where nanodiamonds might be used as photonic switches and tunable lasers.

## Creation of an Antiferromagnetic Exchange Spring



Antiferromagnetic exchange spring. A magnetic field (purple arrow) applied to an FM/AFM bilayer rotates the magnetization.

A. Scholl, M. Liberati, E. Arenholz, H. Ohldag, and J. Stöhr, "Creation of an antiferromagnetic exchange spring," *Phys. Rev. Lett.* **92**, 247201 (2004).

In the ongoing quest for faster and more efficient magnetic data storage, designs for devices such as read heads in computer hard drives are mostly produced through a trial-and-error process, combining thin magnetic films with different properties. To speed up this search for better materials, researchers are striving for a better understanding of the microscopic structure and interactions between ferromagnetic (FM) and antiferromagnetic (AFM) layers. Researchers have now solved a piece of this puzzle using x-ray magnetic linear dichroism (XMLD) spectroscopy and an x-ray magnetometer that allows the rotation of a strong magnetic field in any direction in space. When a ferromagnet and an antiferromagnet are combined in a layered structure — such structures are part of the read heads in computer hard drives — the hard ferromagnet pins and holds the magnetization of the ferromagnet across the interface in the presence of an applied magnetic field, up to a certain field threshold. This pinning, known as exchange bias, results from atomic exchange forces across ferromagnet–antiferromagnet interfaces, which tend to align the magnetization of nearby atoms. When a stronger magnetic field above the threshold is applied, abrupt movement of the ferromagnet is expected, leaving the hard antiferromagnet relatively unaffected. In reality, as the experiments showed, the magnetization of the soft layer dragged the magnetization of the antiferromagnet, winding it like a clock spring. The result is creation of a domain wall between the rotated region at the surface of the sample and the unrotated region below. This behavior is common with ferromagnets but was unknown for antiferromagnets.

### 03: HARD X-RAY SPECTROSCOPY

**OTHER DESIGNATIONS:** Extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray absorption spectroscopy (XAS), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, x-ray absorption near-edge structure (XANES) spectroscopy, x-ray magnetic circular dichroism (XMCD).

**PURPOSE:** Hard x-ray spectroscopy is applied in a wide variety of scientific disciplines (physics, chemistry, life sciences, and geology) to investigate geometric and electronic structure. The method is element-, oxidation-state-, and symmetry-specific. It is a primary tool in the characterization of new and promising materials. It is also used in the elucidation of dilute chemical species of environmental concern.

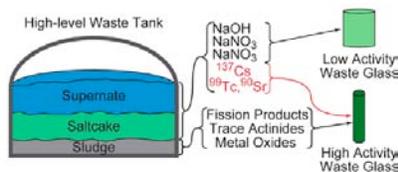
**HOW THE TECHNIQUE WORKS:** In the simplest experimental set-up, the sample is mounted between two detectors, one of which measures the incident radiation and the other measures the transmitted radiation. The ratio of incident and transmitted signals is monitored as the photon energy is swept through element-specific core-level values ("edges"). There are two main variants of the technique depending on the range of the photon-energy sweep.

**EXAFS.** A wide sweep of the photon energy above a core-level edge displays small oscillations in the absorption from which it is possible to deduce nearest-neighbor distances and nearest-neighbor numbers. The photoelectron wave released in the absorption process bounces back to the atom of origin not unlike the "ping" from a submarine sonar.

**NEXAFS.** A narrow sweep near the core-level edge displays characteristic peaks in the spectrum that can serve as a "fingerprint" of the chemical bonding around the atom of origin.

**UNIQUENESS:** The seminal demonstration of the power of EXAFS in the early 1970s by Sayers, Lytle, and Stern has spawned a major scientific industry. The tunability of synchrotron radiation is essential for the sweeps across the core-level edges. The intensity of synchrotron radiation is essential for the detection of dilute species.

## Identification and Control of Radioactive Compounds in Hanford Waste Tanks

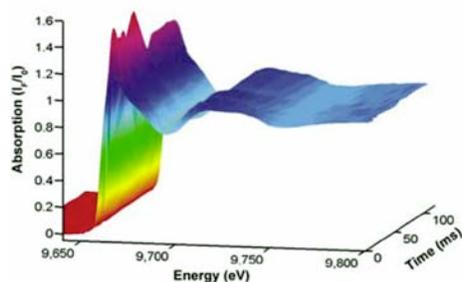


*Outline for vitrification of Hanford high-level waste. Separations are illustrated in red.*

The Hanford nuclear waste site in southeastern Washington State is one of the most contaminated sites in the DOE complex. It stores millions of gallons of radioactive waste from the nation's nuclear weapons programs. High-level radioactive waste is leaking from about a third of Hanford's underground tanks. The waste includes the element technetium in the radioactive form of <sup>99</sup>Tc, which poses a grave threat because of its long half-life (213,000 years) and its potential to contaminate ground water and migrate toward the Columbia River. Radioactive chemicals infiltrating the environment are a cancer hazard to humans. The proposed solution for remediating Tc is to chemically separate it from the tank wastes and store it in solid glass, a process called vitrification. But separating <sup>99</sup>Tc into the proper phase before vitrification is proving difficult in some of the tanks because it forms unknown compounds in some storage conditions. To determine the identity of these unknown <sup>99</sup>Tc compounds in the waste, scientists performed experiments using x-ray absorption spectroscopy, in which x-rays boost electrons in the sample to higher energy states to provide electronic and geometric structural information. Comparison of the experimental results to spectra from known compounds indicates that the unknown species is a Tc(I)-carbonyl complex. These results are extremely valuable because they indicate that technetium separation technologies must be effective for Tc(I)-carbonyl species.

W.W. Lukens, D.K. Shuh, N.C. Schroeder, and K.R. Ashley, "Identification of the non-pertechnetate species in Hanford waste tanks, Tc(I)-carbonyl complexes," *Env. Sci. Tech.* **38**, 229 (2004).

## Interrogating the Silent Zinc Ion in Metalloenzymes

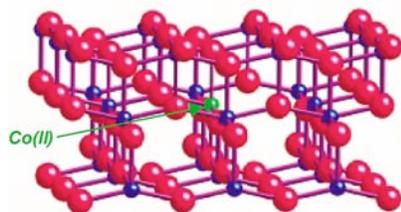


Zinc K-edge EXAFS as function of time.

O. Kleinfeld, A. Frenkel, J.M.L. Martin, and I. Sagi, "Active site electronic structure and dynamics during metalloenzyme catalysis," *Nat. Struct. Biol.* **10**, 98 (2003).

Why do people need zinc in their diets? The metal zinc is an essential mineral that stimulates the activity of approximately 100 enzymes — substances that promote important biochemical reactions crucial to supporting the immune system, healing wounds, and synthesizing DNA. Changes in the local environment of the enzymatic zinc are important for understanding the different steps in the catalytic reaction. Classical enzymology and structural biology have provided insights into the reaction mechanisms of many metalloenzymes. However, little structural information is available on the catalysis of zinc-dependent enzymes, primarily because the zinc ion, with its fully filled 3d orbital, is "silent" for several spectroscopic techniques. Protein crystallography fails when investigating this problem since it depends on stable crystals; it also lacks the resolution to determine whether water molecules participate in the reaction. Using alcohol dehydrogenase from a thermophilic bacterium (*T. brockii*) as a representative zinc metalloenzyme, researchers have applied time-resolved extended x-ray absorption fine structure (EXAFS) spectroscopy to examine the structural and electronic changes that occur at the catalytic site of a zinc metalloenzyme. The results showed a series of changes in the number and distances of atoms surrounding the zinc ion, and these structural changes were reflected in the zinc's effective charge. Furthermore, the data suggested that the enzymatic cycle has six steps, including the addition of a water molecule, the binding of alcohol, the formation of the ketone, and the dissociation of the product. The results emphasized the flexibility of zinc sites during catalysis.

## Room-Temperature Semiconductor for Spintronics



Crystal model shows Co(II) (green) substituting for Ti(IV) (blue) in the lattice, with an oxygen (red) vacancy adjacent to the Co(II).

S.A. Chambers, S.M. Heald, and T. Droubay, "Local Co structure in epitaxial  $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$  anatase," *Phys. Rev. B* **67**, 100401 (2003).

Ferromagnetic semiconductors that remain magnetic at and above room temperature are critical to the development of revolutionary spin-based electronics (or "spintronics"), technologies that manipulate electron spin, in addition to charge, to store and transmit information. Cobalt-doped  $\text{TiO}_2$  anatase is an oxide semiconductor that exhibits ferromagnetism well above room temperature. The thermally robust ferromagnetism is thought to be mediated by electrons from oxygen vacancies created by the substitution of cobalt for titanium (the oxygen vacancy is required to maintain local charge neutrality), but knowledge of the actual mechanism has been elusive. An understanding of the local structure of the magnetic dopant is critical to determining whether the magnetism is caused by elemental cobalt nanocrystals or whether cobalt is a magnetic dopant integrated into the host lattice. The latter is a necessary but insufficient condition for the material being a magnetic semiconductor. X-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopies were used to probe the charge state and local structure of cobalt dopants in  $\text{TiO}_2$  films. The researchers found that there was a significant but incomplete structural correlation between oxygen vacancies and substitutional Co(II) (cobalt in the +2 formal oxidation state). The results established that there was no detectable cobalt metal in the  $\text{TiO}_2$  films. The magnetism was correlated with the presence of substitutional Co(II) in the anatase lattice and free carriers resulting from excess oxygen vacancies. The results support, but do not prove, the contention that cobalt-doped  $\text{TiO}_2$  anatase is a true ferromagnetic semiconductor.

## 04: OPTICS / CALIBRATION / METROLOGY

**PURPOSE:** Integral to the success of several federally funded research programs is the absolute calibration of optical components used for x-ray detection, imaging, and spectroscopy as diagnostics in those programs. It is also important for synchrotron radiation facilities to have some beamline(s) dedicated to the testing and calibration of optics and detectors for use on the other beamlines. O/C/M is used to address several areas in physics and optical instrumentation:

- Nuclear physics (fusion plasma) diagnostics
- Astronomical spectroscopy and imaging, including remote detection of x-rays
- Synchrotron diagnostics and testing of beamline optical components
- Measurement and verification of x-ray optical data

**HOW THE TECHNIQUE WORKS:** Four basic types of x-ray optical components and measurements are considered: detectors (responsivity), mirrors (reflectivity), filters (transmission), and gratings (efficiency). Absolute responsivity (amperes per watt) is measured for test detectors against calibrated standard x-ray detectors that are maintained on site. In some cases, a detector under test may be a two-dimensional array, providing image data. Gratings and mirrors (including multilayers) are calibrated under varying conditions of incident and collection angles, with efficiency or reflectivity given as the ratio of the measured signal to the signal for the incident beam. Similarly, filter calibrations consist of measuring the ratio of x-ray beam intensity with the test component inserted into the beam path to that without.

**UNIQUENESS:** Synchrotron radiation is important for providing high flux onto small optical surfaces, with tunability over an extremely wide range of photon energies. The photon energy range needed, 5 eV to 50 keV, is not available using laboratory x-ray sources. Precision positioning and automation are also important, in particular for angle-resolved or surface-uniformity calibrations of custom components, which must simultaneously be kept in an ultrahigh-vacuum environment. At each beamline, individual calibration standard detectors are maintained, often in collaboration with other laboratories.

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### Characterizing Chandra's Iridium Mirror Coating

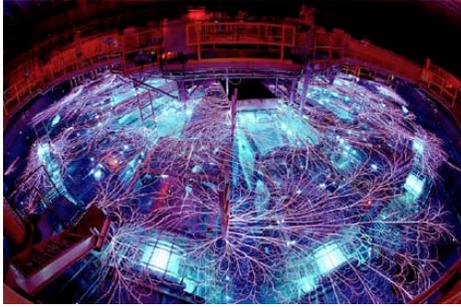


*Chandra X-Ray Observatory with galactic center background (CXC/NGST illustration).*

D.E. Graessle, R. Soufli, A.J. Nelson, C.L. Evans, A.L. Aquila, E.M. Gullikson, R.L. Blake, and A.J. Burek, "Iridium optical constants from synchrotron reflectance measurements over 0.05- to 12-keV x-ray energies," *Proc. SPIE* **5538**, 72 (2004). *Link:* [chandra.harvard.edu](http://chandra.harvard.edu).

NASA's Chandra X-Ray Observatory is a space telescope designed to observe cosmic x-rays from some of the most exotic and explosive environments in the universe: supernovas, quasars, pulsars, and black holes — extreme phenomena that have characterized the universe from the beginning of its existence. To accomplish its mission, Chandra's science support team selected iridium as the coating of choice for the mirrors in its telescope system. However, the use of iridium, a gold-like metal that was found to be the best reflector of x-rays over a wide range of energies, would require a trade-off in the comfort and experience that had already been gained using gold or nickel in previous missions. A portion of this trade-off was to be recovered by means of a separate coating calibration program, wherein a tunable, narrow-bandwidth source (e.g. synchrotron radiation) would be used to characterize the coatings in terms of their optical constants. What ensued was a major programmatic effort to characterize iridium optical constants thoroughly in the energy range of interest, 0.05–12 keV. Hence, in the energy range in question, this material is now understood as well as (or better than) any of its neighboring mirror materials in the periodic table, namely gold, platinum, osmium, rhenium, or tungsten.

### Diagnostics at Z

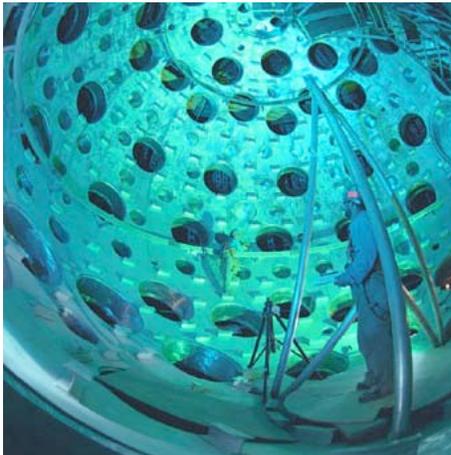


*Z machine at instant of firing (photo by Randy Montoya).*

G.A. Chandler, C. Deeney, M. Cuneo, D.L. Fehl, J.S. McGurn, R.B. Spielman, J.A. Torres, J.L. McKenney, J. Mills, and K.W. Struve, "Filtered x-ray diode diagnostics fielded on the Z accelerator for source power measurements," *Rev. Sci. Instrum.* **70**, 561 (1999).

The "Z" machine at Sandia National Laboratory uses 100-nanosecond, 200-million-ampere pulses of current to generate powerful magnetic fields and x-rays that can be used to simulate nuclear weapon explosions, test materials under extreme conditions, or develop possible technologies for peacetime energy. It is surrounded by an extensive set of diagnostics. Instruments that are routinely used to measure plasma temperature include a filtered five-channel x-ray diode (XRD) array, a filtered six-channel photo-conducting detector (PCD) array, a bolometer, a transmission grating spectrometer, and a filtered silicon photodiode array. Filtered XRD detectors are used as primary radiation flux diagnostics. Vitreous carbon photocathodes are used to reduce the effect of hydrocarbon contamination present in the Z-machine vacuum system. Calibration of these devices is performed periodically (between accelerator shots) to track spectrally dependent changes in the sensitivity of these detectors with exposure to the Z environment. Pre- and postcalibration data taken indicate spectrally dependent changes in the sensitivity of these detectors by factors of up to 2 or 3.

### Diagnostics System for the National Ignition Facility



*The interior of the NIF target chamber, which weighs one million pounds and measures 30 feet in diameter (June 2000).*

R.J. Leeper, G.A. Chandler, et al., "Target diagnostic system for the National Ignition Facility," *Rev. Sci. Instrum.* **68**, 868 (1997).

The National Ignition Facility (NIF) in Livermore, California, is a 192-beam experimental laser facility the size of a sports stadium. The lasers (with 1000 times the instantaneous electric generating power of the United States) focus on a target the size of a BB-gun pellet for a few billionths of a second. Experiments in NIF will allow studies of high-energy-density and fusion regimes with direct applications to stockpile stewardship, energy research, science, and astrophysics. The soft x-ray power diagnostic (SXSS) component of the NIF diagnostic system measures the x-ray emission from a fusion target through a lined hole in its wall, giving the time history of the radiation temperature inside. The diagnostic is based on calibrated x-ray filters, mirrors, and x-ray diodes (XRDs). Transmission gratings may also be used for time-resolved spectroscopy of the NIF shot.

## 05: HARD X-RAY DIFFRACTION

**OTHER DESIGNATIONS:** X-ray diffraction (XRD), powder diffraction, single-crystal diffraction, surface diffraction, x-ray standing wave (XSW).

**PURPOSE:** Essentially everything we know about the atomic structure of materials is based on results from x-ray and neutron diffraction. From advanced ceramics to catalysts, from semiconductor technology to the frontiers of medicine, and from new magnetic materials and devices to framework compounds used to sequester radioactive waste, crystallography using hard x-ray diffraction techniques at synchrotron radiation facilities plays a crucial role in our ability to understand and control the world in which we live. Research problems that this technique can address are:

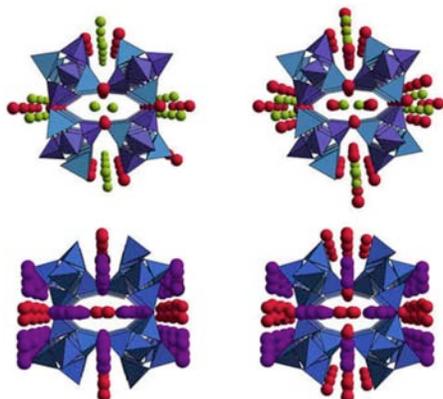
- Structural studies of crystalline materials
- Drug design by pharmaceutical industry
- Biomineralization
- New microporous materials including natrolites, phosphates, and titanates
- Novel complex oxides: structure–property relationships, phase transitions
- Residual stress determination *in situ*

**HOW THE TECHNIQUE WORKS:** Hard x-rays have wavelengths comparable to the distance between atoms. When a crystalline sample is illuminated with x-rays, the x-rays are scattered (diffracted) into very specific directions with various strengths. Detectors are used to measure this “diffraction pattern,” which is then processed by computers to deduce the arrangement of atoms within the crystal. There are two principal modes. In “Bragg” diffraction, the incident x-rays are monochromatic (single wavelength) and the sample is an oriented single crystal. In “Laue” diffraction, the incident x-ray beam is white (all wavelengths) so all the possible diffraction routes are detected.

**UNIQUENESS:** Many materials that can be obtained in single-crystal form are impossible to investigate with laboratory x-ray diffraction equipment because the crystals are too small. Synchrotron hard x-rays provide significant advantages over conventional laboratory sources: increased peak-to-background ratios, angular resolution, and the ability to select photon energies.

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### A Zeolite “Molecular Sponge” to Trap Pollutants?

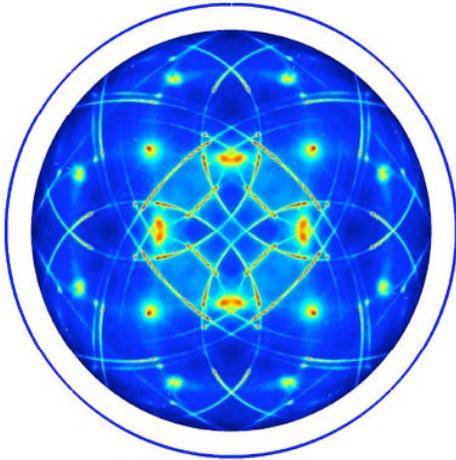


*Polyhedral representations of two zeolites before and after pressure-induced hydration.*

Y. Lee, T. Vogt, J. Hriljac, J. Parise, J. Hanson, and S. Kim, “Non-framework cation migration and irreversible pressure-induced hydration in a zeolite,” *Nature* **420**, 485 (2002).

Zeolites are solids containing aluminum, silicon, and oxygen with regularly spaced pores within the molecular framework. These nanopores make zeolites very useful for trapping small molecules, ions, or gases. It has been previously shown that certain zeolites can expand under pressure and take up more water to become superhydrated. This extra volume allows slightly larger molecules or atoms, such as pollutants, to enter the expanded pores. When the pressure is released and the material contracts, the pollutants would become trapped. However, in a reversible system, half of the water would be expelled again, making the sponges somewhat leaky. Using hard x-ray powder diffraction and single-crystal diffraction, scientists solved the structure of a zeolite (potassium gallosilicate) that exhibits irreversible pressure-induced hydration: when the pressure is released, the material stays superhydrated. The structures obtained show that the irreversible hydration is associated with a rearrangement of the charge-balancing cations contained in the nanopores. By understanding these cation migrations and rearrangements under pressure, scientists may reduce the pressure at which the pressure-induced hydration occurs, and thereby open up new ways to use zeolites as “molecular sponges” for pollutants such as tritiated water or as transport vessels for medical applications.

## Axiotaxy – Discovery of a New Texture in Thin Films

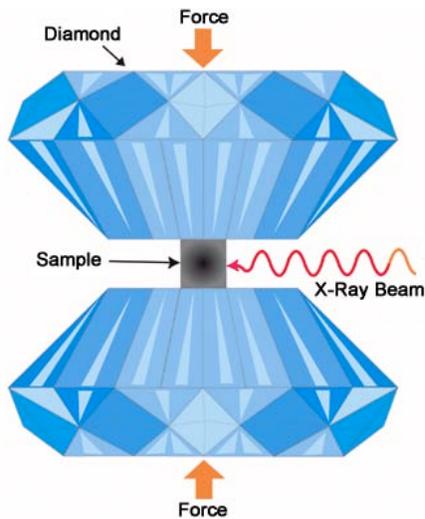


Pole figure for a 60-nm NiSi film on Si(001).

C. Detavernier, A.S. Ozcan, J. Jordan-Sweet, E.A. Stach, J. Tersoff, F.M. Ross, and C. Lavoie, "An off-normal fibre-like texture in thin films on single-crystal substrates," *Nature* **426**, 641 (2003).

At the microscopic level, most materials are made of crystalline grains, and the way these grains fit together is referred to as the material's "texture." The grains can be randomly oriented in three dimensions ("random" texture), randomly oriented within flat layers ("fiber" texture), or neatly arranged and stacked ("epitaxy" texture). The effect of texture on the material's electrical, magnetic, and mechanical properties can be exploited to produce specific characteristics. As the miniaturization of silicon-based devices continues, understanding and controlling texture, which controls the properties of silicides, becomes critical. X-ray diffraction was used to analyze the texture of a nickel silicide (NiSi) thin film on a silicon substrate. The resulting image, called a "pole figure," represents the distribution of the grain orientations in the film. The pole figure obtained for NiSi did not resemble those produced by any of the three known textures or any combination of them. The new texture, named "axiotaxy," is similar to the fiber (layered) texture. However, instead of sitting flat on the substrate, each grain is tilted upwards at the same angle. This causes a special relationship to form between the orientation of the grains in the thin film and the substrate. The mechanism that causes the formation of this new type of texture is unique, and helps us to better understand the physics of thin film growth and phase transformations in thin films.

## Graphite Acts Like Diamond Under Pressure

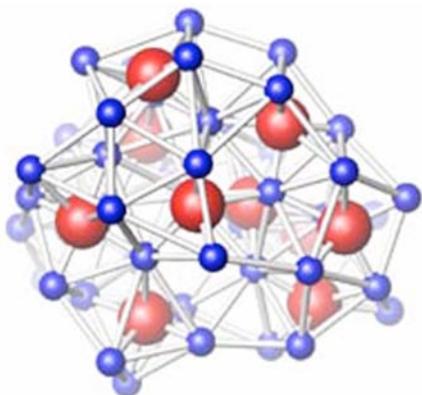


Diamond-anvil cell.

W.L. Mao, H.-K. Mao, P.J. Eng, T.P. Trainor, M. Newville, C.-C. Kao, D.L. Heinz, J. Shu, Y. Meng, and R.J. Hemley, "Bonding changes in compressed superhard graphite," *Science* **302**, 425 (2003).

Researchers have discovered that, under extreme pressure, graphite, among the softest of materials, becomes as hard as diamond, the hardest known material. While graphite is made of loosely bound carbon atoms, diamonds are made of tightly bound carbon atoms, resulting in extreme hardness. These diamond-type bonds are difficult to achieve; natural diamonds are made in the Earth by great pressures and intense heat over geological time scales. The researchers in this study used a diamond-anvil cell to produce pressures approximately 170,000 times the atmosphere at sea level or equal to that more than 300 miles beneath the Earth's surface. The atomic bonds were probed using inelastic x-ray scattering, and structural information was obtained using x-ray diffraction. The findings showed that half of the weak, widely spaced graphite bonds were forced closer together, converting them to stronger, diamond-like bonds. In fact, the graphite became so hard that it cracked the diamond anvil. Moreover, the graphite became optically transparent, a superhard insulator, much like diamond. But, while the known forms of naturally produced diamond retain their hardness, the graphite in this experiment reverted back to its original softness once the pressure was removed. This reversible change in strength offers the possibility of intriguing applications as a pressure-dependent structural component (for instance, a composite gasket for a high-pressure apparatus).

## Looking into Glass's Secrets

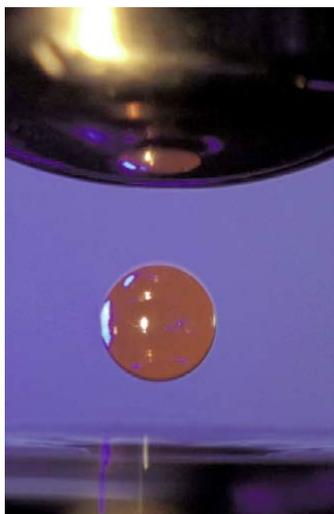


*Octahedral structure of germania glass at 100,000 times atmospheric pressure.*

M. Guthrie, C.A. Tulk, C.J. Benmore, J. Xu, J.L. Yarger, D.D. Klug, J.S. Tse, H-K. Mao, and R.J. Hemley, "Formation and structure of a dense octahedral glass," *Phys. Rev. Lett.* **93**, 115502 (2004).

Little is known about the structure of glass under pressure, even though we use it in our cars, our homes, and industry. It is difficult to study because, on the atomic level, glass is disordered; it lacks a periodic crystal structure. Researchers used a combination of tools, including neutron and x-ray diffraction, to study how the structure of glass changes under high pressures. Germania, a structural analogue to the more common form of silica glass, was used because it transforms structurally at much lower pressures and provides a greater contrast in neutron and x-ray techniques. At ambient pressure, glass is made up of tetrahedral units: four oxygen atoms enclose a germanium atom to create cages that are only a nanometer across. While neutron studies are sensitive to lighter elements such as oxygen, x-ray studies reveal germanium atoms more clearly and can test smaller samples, allowing studies at higher pressures. The researchers found that, as the sample was pushed from 60,000 to 150,000 times ambient pressure, the tetrahedral cages collapsed, and an average of five oxygen atoms organized around the germanium atom before the final, dense, purely octahedral form that has eluded scientists for decades was observed. This provided evidence that germania glass undergoes a continuous structural transformation, disproving the theory that tetrahedral glasses go through a distinct transition between low- and high-density phases. In addition, they found that the angles of the structures were not the 90 and 180 degrees of a perfect octahedron; instead, the angles were near 90 and 165 degrees.

## Levitated Droplets Reveal Origin of Undercooling



*Electrostatically levitated droplet of molten Ti-Zr-Ni.*

K.F. Kelton, G.W. Lee, A.K. Gangopadhyay, R.W. Hyers, T.J. Rathz, J.R. Rogers, M.B. Robinson, and D.S. Robinson, "First x-ray scattering studies on electrostatically levitated metallic liquids: Demonstrated influence of local icosahedral order on the nucleation barrier," *Phys. Rev. Lett.* **90**, 195504 (2003).

For over 50 years, it has been known that, under carefully controlled conditions, metallic liquids can be cooled far below their melting temperatures (undercooled) before crystallizing. This suggests that the mechanism responsible for forming the solid phase must present a large barrier to phase change. To explain this surprising result, F.C. Frank theorized that as metallic liquids cool, local structures with icosahedral (20-sided) symmetry develop that are incompatible with the long-range periodicity of the crystalline phase. Several experimental studies have supported this hypothesis but have shopped short of providing direct proof. Using an electrostatic levitation technique that allows in situ x-ray diffraction of a liquid-metal droplet in a containerless environment, researchers for the first time directly confirmed Frank's hypotheses by studying the undercooling behavior of the liquid metal Ti-Zr-Ni. High-energy x-rays were required to penetrate the droplet to collect x-ray diffraction data in a transmission mode. The researchers measured increasing icosahedral short-range order (ISRO) in the liquid as it was undercooled, finding that this was responsible for the nucleation of a metastable icosahedral quasicrystal phase instead of the stable polytetrahedral phase. This verifies Frank's hypothesis and demonstrates that local order in the liquid phase strongly influences the nucleation of specific phases, even in metallic liquids, where atomic interactions are weak and relatively isotropic.

## 06: MACROMOLECULAR CRYSTALLOGRAPHY

**OTHER DESIGNATIONS:** Protein crystallography (PX).

**PURPOSE:** PX is the most powerful method for the determination of the three-dimensional structure of large biological molecules (macromolecules). Areas addressed include:

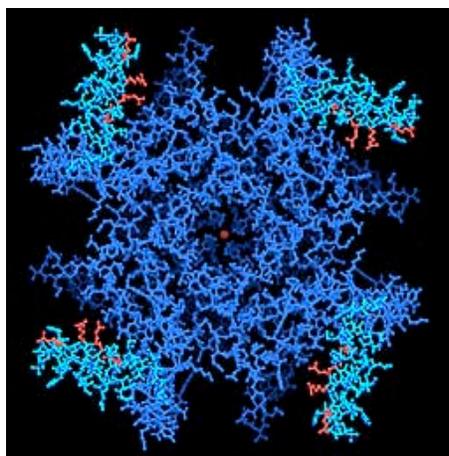
- Therapeutic drug design
- Enzyme mechanisms
- Supramolecular structure
- Molecular recognition
- Nucleic acids
- Structural genomics
- High-throughput crystallography

**HOW THE TECHNIQUE WORKS:** X-rays are passed through crystals of the macromolecule under study. The x-rays are scattered by the atoms of the crystal, producing a diffraction image that gives information on the structure of the crystals. In multiwavelength anomalous diffraction (MAD), x-rays of different wavelengths are used on the same crystal to detect small variations in the diffraction intensity at different energies due to the presence of a heavy atom. This provides information about the relative phases of the diffracted beams, crucial for reconstructing an image of the molecule and without which additional measurements must be made or some prior structural knowledge exploited.

**UNIQUENESS:** Because macromolecules are large and flexible, their crystals tend to be small, imperfect, and weakly diffracting. In many cases, the intensity, small beam size, and collimation of a synchrotron beam is vital for successful results. The MAD phasing method also requires tunability of wavelengths. Because MAD uses only a single crystal and can provide phases very rapidly, it is a popular technique among crystallographers today, and beamlines optimized for these experiments are among the most oversubscribed.

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### A Membrane Protein Structure Worthy of a Nobel Prize

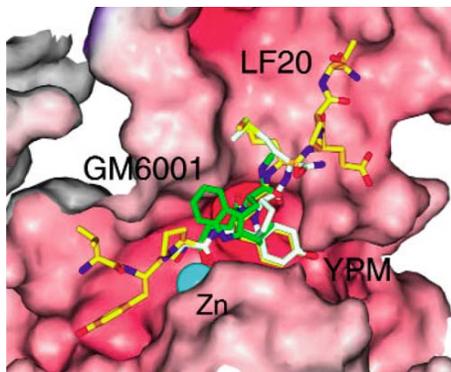


*Overhead view of a voltage-dependent potassium ion channel.*

Y. Jiang, A. Lee, J. Chen, V. Ruta, M. Cadene, B.T. Chait, and R. MacKinnon, "X-ray structure of a voltage-dependent K<sup>+</sup> channel," *Nature* **423**, 33 (2003).

Virtually all communication between a cell and its environment is mediated by membrane proteins. They are critical in a variety of biological functions, including photosynthesis, vision, neural transmission, pathogenesis, and drug resistance. Membrane proteins control the electrochemical potentials that generate nerve impulses, transduce the signaling functions of hormones, and even generate adenosine triphosphate (ATP) — the cell's source of energy. Even though they represent approximately 30% of proteins coded by genomes, they are dramatically underrepresented in the Protein Data Bank. They are notoriously difficult to crystallize. Synchrotron x-ray sources are essential for making advances in this field. Work on the voltage-dependent potassium channel, awarded the 2003 Nobel Prize for chemistry, is a perfect example of the dramatic impact that structural studies of membrane proteins have in the understanding of cellular function. Certain membrane proteins open and close to regulate ion conduction in response to changes in cell-membrane voltage. These "life transistors" help to control electrical activity in muscles and nerves. The structure, showing 4 red-tipped "paddles" that open and close in response to positive and negative charges, answers the question of how this kind of channel functions as a voltage-dependent switch, driving muscle and nerve activity in all living organisms.

## Anthrax Toxin – Working Toward an Antidote

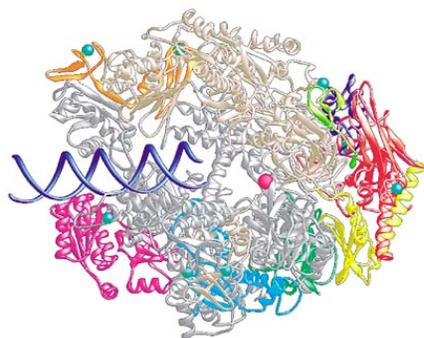


Close-up view of anthrax lethal factor in complex with a peptide and two inhibitors.

R.G. Panchal, A.R. Hermone, T.L. Nguyen, T.Y. Wong, R. Schwarzenbacher, J. Schmidt, D. Lane, C. McGrath, B.E. Turk, J. Burnett, M.J. Aman, S. Little, E.A. Sausville, D.W. Zaharevitz, L.C. Cantley, R.C. Liddington, R. Gussio, and S. Bavari, "Identification of small molecule inhibitors of anthrax lethal factor," *Nature Structural & Molecular Biology* **11**, 67 (2004).

Anthrax makes a deadly cocktail of three toxin proteins that flood the bloodstream, leading to rapid death if the infection is not treated in its early stages. Even antibiotic treatments can fail when the anthrax bacterium, *Bacillus anthracis*, has already produced lethal levels of toxins. The poisonous protein called lethal factor (LF) rapidly blocks signals to recruit immune cells to fight the infection. Another enzyme, edema factor (EF), causes the release of fluid into the lungs and is deadly on its own. Protective antigen (PA) facilitates the entry of these toxin proteins across the cell membrane, and into target cells, through its complex pore-forming channel. LF is the greatest source of damage in highly fatal cases of inhalation anthrax. An antitoxin that stops LF would be a vital addition to combined therapy with existing treatments (antibiotics, anti-PA antibodies, critical care). Scientists have taken a big step forward in developing a drug to inhibit the LF toxin. Small molecules were screened to identify chemical compounds that can block LF. Crystals of LF bound to these candidate inhibitors were made and x-ray crystallography was used to analyze the interactions of these compounds with LF. The research concluded that the most effective inhibitors targeted the active center via hydrophobic interactions and also deprived LF of zinc.

## Enzyme Structure Helps Unravel Mysteries of DNA

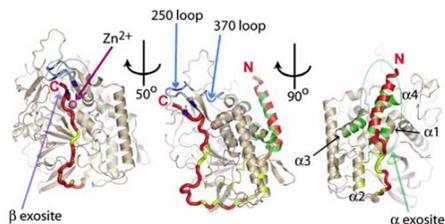


Ribbon diagram of RNA polymerase II backbone model.

P. Cramer, D.A. Bushnell, J. Fu, A.L. Gnatt, B. Maier-Davis, N.E. Thompson, R.R. Burgess, A.M. Edwards, P.R. David, and R.D. Kornberg, "Architecture of RNA polymerase II and implications for the transcription mechanism," *Science* **288**, 640 (2000).

Before a cell can begin to divide or differentiate, the genetic information within the cell's DNA must be copied, or "transcribed," onto complementary strands of RNA. RNA polymerase II (pol II) is an enzyme that, by itself, can unwind the DNA double helix, synthesize RNA, and proofread the result. When combined with other molecules that regulate and control the transcription process, pol II is the key to successful interpretation of an organism's genetic code. However, the size, complexity, scarcity, and fragility of pol II complexes have made analysis of these macromolecules by x-ray crystallography a formidable challenge. A team of structural biologists has met this challenge using data obtained from synchrotron facilities. The resultant high-resolution model of a 10-subunit pol II complex suggests roles for each of the subunits and will allow researchers to begin unraveling the intricacies of DNA transcription and its role in gene expression.

## The Many Faces of Botulinum Neurotoxin

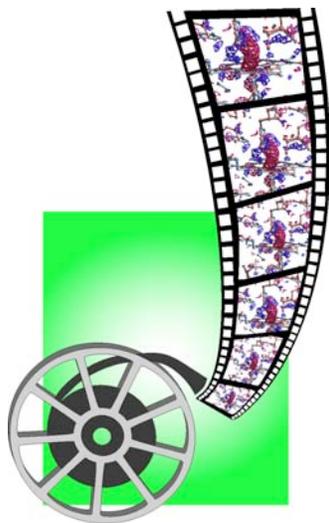


Three different views of the CNT–SNARE complex.

M.A. Breidenbach and A.T. Brunger, "Substrate recognition strategy for botulinum neurotoxin serotype A," *Nature* **432**, 925 (2004).

Botox® face lifts and botulism disease are both based on a neurotoxin from the bacterium *Clostridium botulinum*. The toxin, often described as the most lethal substance known, is a member of the clostridal neurotoxins (CNTs) group, which block muscle contractions. When injected into a person's face, the effect is a lessening of wrinkles. When ingested, the toxin paralyzes muscles, including those of the internal organs, causing sickness and death. The toxin is also used in medicine for conditions such as uncontrolled blinking, lazy eye, and involuntary muscle contractions. Nerve cells cause muscles to move by delivering the neurotransmitter acetylcholine into muscle cells. CNTs paralyze muscles by blocking acetylcholine delivery. CNTs enter nerve cells then find and cut SNARE proteins, the machinery responsible for acetylcholine delivery. The inactivation of nerve cells lasts for three to six months. Scientists have solved the first crystal structure of a CNT bound to a SNARE. They found extensive contact between the toxin and its target. In kinetic experiments based on the crystal structure, the authors found that the toxin wraps the target SNARE protein around itself. This ensures both target specificity and proper positioning for cutting the SNARE. Knowing the structure of the CNT–SNARE interaction furthers understanding of the toxin's mechanism and may lead to drugs that can treat CNT poisoning.

## Molecular Movies – The Time-Resolved Structure of Myoglobin



Time-resolved crystallography enables the capture of myoglobin "movie" sequences.

V. Srajer, Z. Ren, T.-Y. Teng, M. Schmidt, T. Ursby, D. Bourgeois, C. Pradervand, W. Schildkamp, M. Wulff, and K. Moffat, "Protein conformational relaxation and ligand migration in myoglobin: A nanosecond to millisecond molecular movie from time-resolved Laue x-ray diffraction," *Biochemistry* **40**, 13802 (2001).  
Link: [moffat.bsd.uchicago.edu](http://moffat.bsd.uchicago.edu).

Crystallographers are no longer confined to static observations of protein structures. The availability of extremely intense, multiwavelength, pulsed synchrotron x-ray sources has reduced exposure times enough to capture "movie sequences" of fundamental molecular processes. This approach has been applied to studies of myoglobin, the iron-based molecule responsible for oxygen transport in muscles. Absorption of a photon by myoglobin breaks a bond between the central iron atom and a carbon monoxide molecule, initiating a series of spectroscopic and structural changes, ultimately followed by rebinding of the carbon monoxide. The entire photolysis, relaxation, and rebinding processes occur in less than 5 milliseconds at room temperature. To observe this, the carbon monoxide was photodissociated by a 7.5-nanosecond laser pulse, and the subsequent structural changes were probed by 150-picosecond or 1-femtosecond x-ray pulses at delay times ranging from 1 nanosecond to 1.9 milliseconds. Researchers are now extending this approach to several other light-sensitive signaling systems that are chemically and biologically diverse and are developing new techniques that will enhance the time resolution from the nanosecond range, first to a few hundred picoseconds and perhaps ultimately to femtoseconds.

## 07: HARD X-RAY SCATTERING

**OTHER DESIGNATIONS:** Small-angle x-ray scattering (SAXS), wide-angle x-ray scattering (WAXS), grazing-incidence small-angle x-ray scattering (GISAXS), x-ray Raman scattering, Compton scattering, inelastic x-ray scattering (IXS), resonant inelastic x-ray scattering (RIXS), nuclear resonant scattering (NRS), x-ray photon correlation spectroscopy (XPCS).

**PURPOSE:** Hard x-ray scattering techniques represent a broad extension of x-ray diffraction methods to the enormous range of systems that are not perfectly ordered or static. Problems addressed include:

- Liquid–vapor, liquid–liquid, and molecular film interfaces
- Colloids, solution-phase proteins, polymers
- Collective dynamics in soft materials
- Short-range order in amorphous materials
- Phonons and elementary excitations in solids
- Electron momentum distribution in solids

**HOW THE TECHNIQUE WORKS:** Monochromatic x-rays (single wavelength, single energy) impinge upon the sample of interest. The scattered x-rays are detected and their intensities are measured as a function of the angle of scattering. The angular range can be small as in SAXS (low momentum transfer) or wide as in WAXS (high momentum transfer). There are two principal variants of the technique:

- (1) Elastic. The energy (wavelength) of the detected x-ray is the same as that of the incident x-ray.
- (2) Inelastic. The energy of the detected x-ray is lower than that of the incident x-ray. The lost energy is carried away by a vibrational, electronic, or magnetic excitation. The detection system in this case requires a spectrometer to measure the energy loss.

**UNIQUENESS:** The high intensity of synchrotron radiation permits the study of dilute samples where the atoms of interest constitute only one-millionth or less of the total population. The accessible range of momentum transfer is very favorable. Time-resolved SAXS/WAXS studies on systems such as polymer phase formation and mechanical processing are enabled. Tunability is essential for RIXS, a unique probe of atomic-orbital ordering. Highly coherent x-rays are essential for XPCS studies of the dynamics of small particles, information that cannot be obtained in any other way.

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### Transport Properties of Molten Aluminum Oxide

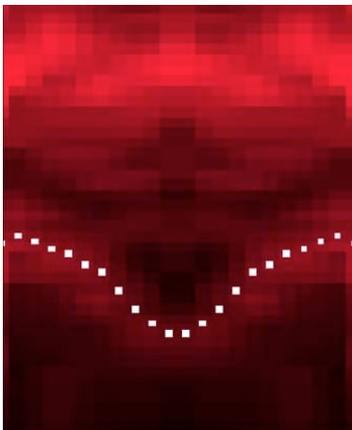


*Levitated liquid aluminum oxide sample in a super-cooled state at ~1800° C.*

H. Sinn, B. Glorieux, L. Hennet, A. Alatas, M. Hu, E.E. Alp, F.J. Bermejo, D.L. Price, and M.-L. Saboungi, "Microscopic dynamics of liquid aluminum oxide," *Science* **299**, 2047 (2003).

The transport properties (such as viscosity or thermal conductivity) of high-temperature oxide melts are of considerable interest for a variety of applications, including modeling the Earth's mantle, optimizing aluminum production, confining nuclear waste, and investigating the use of aluminum in aerospace propulsion. However, it is difficult to obtain data on the microscopic transport properties of high-temperature liquid oxides because the chemical reactivity of the material precludes the use of traditional containers. In addition, kinematic restrictions on neutron scattering make it impossible to study acoustic modes of energy absorption, and black-body radiation restricts the utility of (visible) light scattering. Researchers have sought to circumvent these limitations by studying aluminum oxide using high-resolution inelastic x-ray scattering. Molten spheres 3–4 mm in diameter were suspended in an oxygen gas jet, allowing a clear path for the incident and scattered x-ray beams. The spectra obtained when the x-rays were widely scattered (high-Q spectra) were well described by theory, but the spectra in the cases where the x-rays were more narrowly scattered (low-Q spectra) diverged significantly from hydrodynamic theory. The low-Q spectra require a frequency-dependent viscosity and impose previously unknown experimental constraints on the behavior of liquids.

## Direct Evidence of Holons in Strontium Copper Oxide

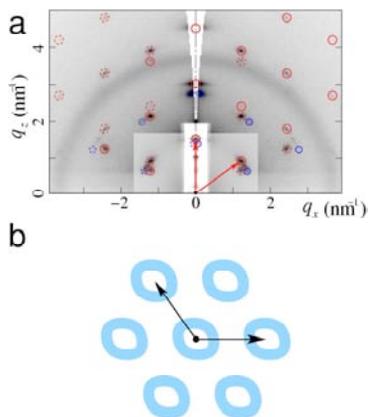


Energy vs momentum plot (red indicates high spectral intensity). The necklace feature corresponds to a holon-antiholon spectrum.

M.Z. Hasan, Y-D. Chuang, Y. Li, P. Montano, M. Beno, Z. Hussain, H. Eisaki, S. Uchida, T. Gog, and D.M. Casa, "Direct spectroscopic evidence of holons in a quantum antiferromagnetic spin-1/2 chain," *Int'l. J. Mod. Phys. B* **17**, 3479 (2003).

High-temperature superconductivity in cuprate materials, colossal magnetoresistance in manganates, and unusually intense nonlinear optical responses in nickelates are all phenomena thought to result from very strong interactions among electrons. According to theory, some of these compounds should also exhibit other unusual physical properties, such as charge fluctuations in the form of exotic quanta called "holons." To examine this phenomenon, a method sensitive to valence-band excitations must be employed. Researchers used resonant inelastic x-ray scattering (RIXS) to obtain direct evidence of holons in a strontium copper oxide antiferromagnet. In earlier work, the researchers demonstrated that tuning the incident x-ray energy near an absorption edge results in a large enhancement of the valence-band scattering, making possible detailed momentum-resolved studies of high-Z materials. In addition, because of the high brightness of third-generation synchrotrons, scattering studies over the entire Brillouin zone were feasible. Features in the inelastic x-ray scattering spectra indicate a particle-hole excitation and comparison with numerical studies shows good agreement with holon formation. Considered together, these observations are consistent with the presence of spin-charge separation and the formation of holons and antiholons in this cuprate. Future efforts, perhaps feasible at high-brightness facilities, may allow much higher resolution experiments that can capture the full range of spin-charge behavior in these interesting materials.

## Model Lipid Membranes Help Demystify Membrane Fusion

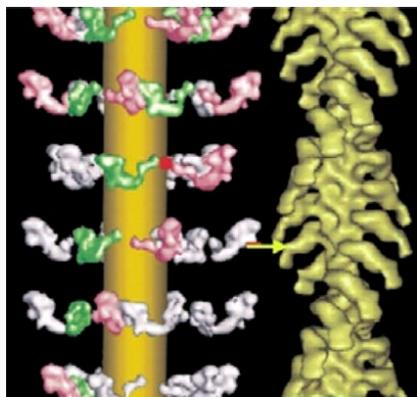


The diffraction pattern (a) from the distorted hexagonal phase suggests that the lipid might have formed distorted tubes (b).

L. Yang and H.W. Huang, "Observation of a membrane fusion intermediate structure," *Science* **297**, 1877 (2002); L. Yang, L. Ding, and H.W. Huang, "New phases of phospholipids and implications to the membrane fusion problem," *Biochemistry* **42**, 6631 (2003).

Cellular membrane fusion is one of the most common ways for molecules to enter or exit cells. Understanding the details of membrane fusion may help scientists prevent viruses such as HIV from fusing to and thereby infecting human cells; it may also lead to the design of systems facilitating drug delivery or gene therapy. The primary structural component of a cellular membrane is a double layer of lipid molecules. To understand how structural transitions such as fusion occur, researchers used x-ray diffraction to study the transition from planar lipid layers (lamellar phase) to hexagonally stacked lipid tubes (inverted hexagonal phase). The experiments were performed on model membranes that were made of hundreds of lipid bilayers on a silicon substrate. The composition of the samples was varied along with temperature and water content. The results showed that, when a binary lipid mixture (DOPC/DOPE) was dehydrated, a new lipid structure was found. Though resembling the well-known hexagonal phase structure in which the lipids form circular tubes, the lipids in this new structure appear to form noncircular tubes that stack into a distorted hexagonal lattice. This implies that under the mechanical stress induced by dehydration, the two lipid species in the mixture might demix so as to lower the overall free energy of the system, a mechanism that might be utilized in membrane fusion to lower the free energy barriers in the fusion pathway.

## Grasping the Structure of Insect Muscle

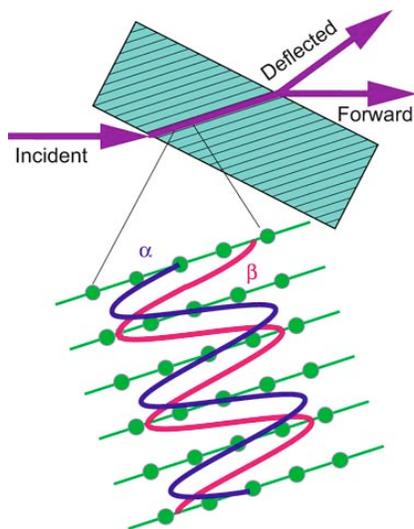


*Myosin heads in their pre- and post-powerstroke state.*

H.A. Al-Khayat, L. Hudson, M.K. Reedy, T.C. Irving, and J.M. Squire, "Myosin head configuration in relaxed insect flight muscle: X-ray modeled resting cross-bridges in a pre-powerstroke state are poised for actin binding," *Biophys. J.* **85**, 1063 (2003).

Researchers have achieved the first detailed view of resting muscle filaments poised to contract, a long-sought window into the biochemical cycle that causes muscle contraction. Muscle fibers contain two sets of protein filaments, made of myosin and actin, that "telescope" past each other to stretch or shorten the muscle. The shortening motion is driven by myosin "heads" that bind to, bend against, and then release adjacent actin filaments (a "powerstroke"). Researchers had previously viewed the end state of the powerstroke, but no one had reported the orientation of the unbound heads in myosin's relaxed initial state until recently. Researchers recorded low-angle x-ray diffraction patterns from flight muscle fibers of giant waterbugs. The results confirmed that resting myosin filaments have stacked rings or "crowns" of eight heads each — two heads per myosin molecule. One head of each myosin projects about 90° from the filament axis; the other tucks inward. Each of the four projecting heads rotates slightly about the "neck," which connects to a pivot on the myosin filament. The rotation positions the head to bind tightly to the actin filament and tilt forcefully by 45° relative to the axis of the filament. Such a powerstroke would move the head and bound actin filament 10 nanometers down the axis. The four inward-pointing heads each touch an adjacent projecting head. These contacts may restrain both myosin heads from cleaving adenosine triphosphate (ATP) molecules — the powerstroke fuel — until the right moment. As if optimized to do so, the relaxed outward myosin heads seem poised to bind actin and begin powerstroking.

## A Switch in Time — Coherent Control of Pulsed X-Ray Beams



*Geometry for a subpicosecond x-ray switch.*

M.F. Decamp, D.A. Reis, P.H. Bucksbaum, B. Adams, J.M. Caraher, R. Clarke, C.W.S. Conover, E.M. Dufresne, R. Merlin, V. Stoica, and J.K. Wahlstrand, "Coherent control of pulsed x-ray beams," *Nature* **413**, 825 (2001).

Tracking changes in molecular structure during chemical and biochemical reactions requires the ability to switch hard x-ray beams on and off rapidly enough to capture the motion of the atoms (a subpicosecond time scale). An elegantly simple and highly adaptable x-ray "switch" uses vibrations in a crystal to modulate the transmission of coherent x-ray pulses. The switch consists of a specially cut and aligned germanium crystal placed in the path of the synchrotron x-ray beam to produce two diffracted beams. The crystal is also coherently excited by a femtosecond laser pulse, resulting in lattice vibrations that transiently rearrange the atoms in the crystal. Inside the crystal, the x-ray beam consists of two standing waves: the  $\alpha$ -wave has its nodes on the atomic planes and thus experiences low absorption, while the  $\beta$ -wave has its antinodes on the atomic planes and thus experiences enhanced absorption. This affects the transmission of the incident x-ray beam, redistributing energy between the two exiting beams. By simply varying the time delay between the x-rays and the laser, researchers can switch the exiting beams on and off or change their relative strengths. An even faster switch might result from perturbation of the electron distribution around atoms in the crystal lattice or through the use of optical rather than acoustic modes of lattice vibration (one period is typically about 30 femtoseconds).

## 08: SOFT X-RAY SCATTERING

**OTHER DESIGNATIONS:** Soft x-ray emission spectroscopy (SXES), inelastic x-ray scattering (IXS), resonant x-ray inelastic scattering (RIXS), speckle patterns, small-angle x-ray scattering (SAXS).

**PURPOSE:** Soft x-ray scattering techniques employ the excitation of electrons in relatively shallow core energy levels (100–2000 eV) to probe the electronic structure and other properties of various kinds of matter. Problems addressed by soft x-ray spectroscopic techniques include:

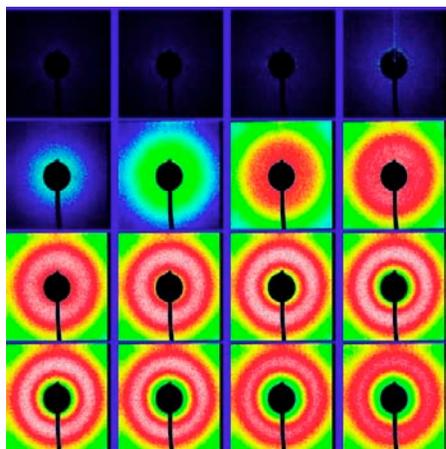
- Strongly correlated materials
- Magnetic materials
- Environmental science
- Catalysis

**HOW THE TECHNIQUE WORKS:** Soft x-ray scattering is a photon-in/photon-out technique. The sample is illuminated with monochromatic soft x-rays and the scattered photons are detected over a small angular range. In the elastic scattering mode one measures the speckle diffraction pattern. In the inelastic mode the scattered photons are passed through a spectrometer and analyzed. Additional information is obtained in the resonant condition when the incident photon is near a core-level-energy absorption edge.

**UNIQUENESS:** Each element has its own set of characteristic core-electron energies, giving these techniques their elemental specificity. The tunability of synchrotron radiation is essential. Because of the low cross sections involved, SXES and RIXS are viable only at brilliant synchrotron sources.

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### Learning How Magnets Forget

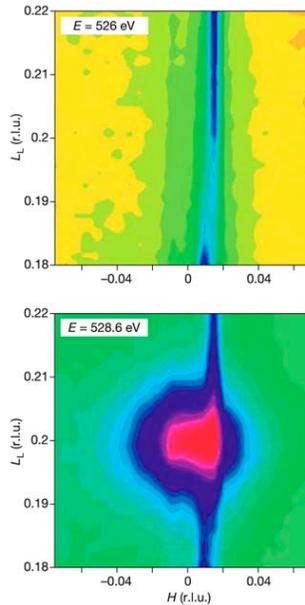


*Magnetic speckle pattern evolves from the featureless configuration in the magnetically saturated region of the hysteresis curve to the annular shape characteristic of a two-dimensional liquid of interacting domains at zero field.*

M.S. Pierce, R.G. Moore, L.B. Sorensen, S.D. Kevan, O. Hellwig, E.E. Fullerton, and J.B. Kortright, "Quasistatic x-ray speckle metrology of microscopic magnetic return-point memory," *Phys. Rev. Lett.* **90**, 175502 (2003).

A magnetic material immersed in an external magnetic field has a magnetization. As the external field cycles between positive and negative values, the magnetization traces out a hysteresis loop. While hysteresis underlies all magnetic data-storage technology, it is not understood at the microscopic level. Nevertheless, the magnetic disk drive industry has had a cumulative growth rate for the past decade that dwarfs even the celebrated Moore's Law growth rate for microcircuits. A number of technological innovations have made this growth possible, including the use of thin layers of magnetic materials into which a certain amount of disorder has been introduced in a controllable way. Scientists have developed an x-ray analogue of the laser speckle well known to anyone who has seen the pattern created when laser light strikes a dusty mirror. They have used their technique to track quantitatively the evolution of magnetic domains as the magnetic layer cycles through various hysteresis loops, thereby directly probing how hysteresis unfolds at the microscopic level. They discovered that, contrary to the best current theories, the disordered magnetic storage materials partially remember their microscopic domain configuration, even after saturation.

## "Hole Crystal" Phase in the Spin Ladder of SCO

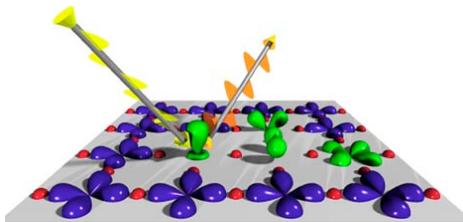


Experimental signature of a hole crystal phase for x-ray energies both off (top) and on (bottom) the ladder resonance.

P. Abbamonte, G. Blumberg, A. Rusydi, A. Gozar, P.G. Evans, T. Siegrist, L. Venema, H. Eisaki, E.D. Isaacs, and G.A. Sawatzky, "Crystallization of charge holes in the spin ladder of  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ ," *Nature* **431**, 1078 (2004).

Determining the nature of the electronic phases that compete with superconductivity in high-transition-temperature (high- $T_c$ ) superconductors is one of the deepest problems in condensed matter physics. One candidate is the "stripe" phase in which the charge carriers (holes) condense into rivers of charge that separate regions of antiferromagnetism. A related but lesser known system is the "spin ladder," which consists of two coupled chains of magnetic ions connected by an array of rungs. Doped ladders have been predicted to exhibit both superconductivity and an insulating "hole crystal" phase in which the charge-carrying holes are localized through many-body interactions. One use of soft x-ray scattering is to identify such previously "hidden" electronic phases. Using a soft x-ray scattering technique in which scattering from holes is selectively enhanced more than a thousandfold, scientists have reported the existence of a hole crystal in the doped spin ladder of SCO ( $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ ). This phase exists without a detectable distortion in the structural lattice, indicating that it arises from many-body electronic effects. The measurements confirmed theoretical predictions and supported the picture that proximity to charge-ordered states is a general property of superconductivity in copper oxides.

## How Much Energy Does It Cost to Tilt a Hole?



In Raman scattering, the absorption and emission of an x-ray result in the excitation of the copper orbital from the ground state (blue) to an excited state with a different orientation (green).

One signature of the onset of superconductivity is the formation of electron pairs, but the electron-pairing mechanism for high-temperature superconductivity is one of the great unsolved problems of condensed-matter physics. The common feature of high-temperature superconductors is a set of parallel copper-oxygen planes. In these planes, each  $\text{Cu}^{2+}$  ion is surrounded by four oxygen atoms. The  $\text{Cu}^{2+}$  ions have an unoccupied electron orbital called a hole. We know from the angle dependence of x-ray absorption that this hole orbital is oriented in the plane with four lobes pointing toward the four neighboring oxygen atoms. Putting the hole in a differently oriented orbital costs energy. How large these energies are is a potentially important question for the theory of high-temperature superconductivity. If these energies are small (comparable to the thermal energy), excitations to these orbitals should be considered in whatever electron-pairing mechanism is operative in superconductivity. Scientists have used resonant x-ray Raman scattering to investigate electronic transitions within copper atoms in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , an insulating model compound for the copper-based high-temperature superconductors. Contrary to earlier conjecture, they found that these transitions have energies that are too high to be directly involved in the electron-pairing mechanism.

P. Kuiper, J.-H. Guo, C. S  the, L.-C. Duda, J. Nordgren, J.J.M. Pothuizen, F.M.F. de Groot, and G.A. Sawatzky "Resonant x-ray Raman spectra of Cu dd excitations in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ," *Phys. Rev. Lett.* **80**, 5204 (1998).

## 09: HARD X-RAY IMAGING

**OTHER DESIGNATIONS:** Radiography, phase contrast imaging, scanning micro/nanoprobe, full-field microscopy, diffraction enhanced imaging (DEI), x-ray tomography, topography.

**PURPOSE:** Hard x-ray imaging nondestructively visualizes samples, frequently the internal or hidden components of the samples. It is applicable to nearly all fields of science from the life sciences to engineering to archaeology. A few uses are:

- Human and animal physiology (amplitude- or phase-contrast imaging and DEI)
- Mapping of magnetic domains in two dimensions (micro/nanoprobe)
- Mapping of composite materials in three dimensions (tomography)
- Properties of individual grains in a polycrystalline material (micro/nanoprobe)
- Mapping of the distribution of elements in cells (micro/nanoprobe)
- Strains in near-perfect crystals (diffraction imaging topography)
- Time-resolved imaging of sprays (radiography)

**HOW THE TECHNIQUE WORKS:** There are two basic experimental methods:

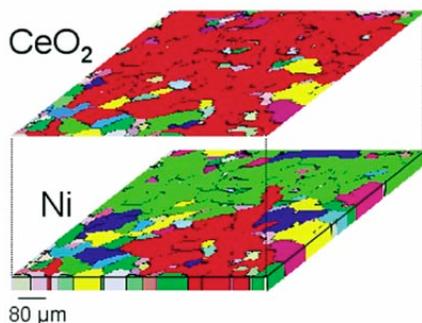
- (1) Imaging. A full-field image can be recorded, not unlike the images taken by your doctor or dentist.
- (2) Scanning. A very small illuminated spot is created on the sample using focusing devices. The image is then built up by "raster scanning" the sample through the illuminated spot.

In either case, there has to be a physical cause of the contrast. This can be due to changes in absorption, elemental composition, or refractive index of the sample.

**UNIQUENESS:** What are the relative merits of x-ray microscopes and electron microscopes? Electron microscopes will always have better spatial resolution, but they will be limited in the range of samples that can be studied. The uniqueness of x-ray imaging resides in its deeper penetration, enabling the study, for example, of buried interfaces and wet biological samples.

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### Growth Modes of Oxide Films on Textured Metal Substrates

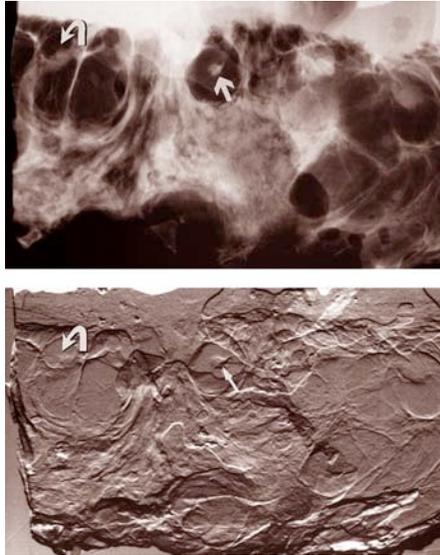


*Orientation maps from a deposited oxide film and a textured nickel substrate obtained from x-ray Laue microdiffraction.*

J.D. Budai, W. Yang, N. Tamura, J.-S. Chung, J.Z. Tischler, B.C. Larson, G.E. Ice, C. Park, and D.P. Norton, "X-ray microdiffraction study of growth modes and crystallographic tilts in oxide films on metal substrates," *Nat. Mater.* **2**, 487 (2003).

Interactions between small, tightly packed single crystals at their boundaries ultimately determine the structural and electronic behavior of most polycrystalline materials. X-ray microbeam studies of individual grains can now characterize the local three-dimensional structure, orientation, and strain with submicrometer resolution, as demonstrated in epitaxially grown cerium oxide ( $\text{CeO}_2$ ) films on textured nickel (Ni) substrates. Understanding the microstructure of such heteroepitaxial materials is crucial to the development of superconductor technology based on deposited films. Analysis of diffraction patterns revealed two distinct growth regimes, and large-area orientation mapping showed that crystallographic tilting associated with the complex interfaces gave rise to enhanced texture. The tilt mechanisms should apply to many oxide/metal systems, including thermal barrier coatings, solar cells, and interfaces in electronic devices, suggesting that the benefits of intentionally enhanced texture are achievable in many coated materials.

## Diffraction-Enhanced Imaging Improves Cancer Detection

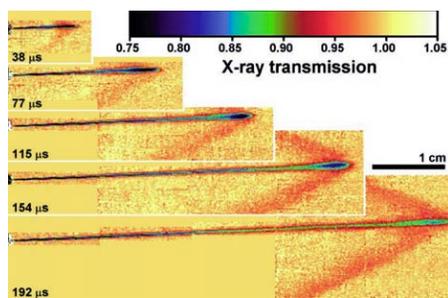


Digital radiograph (top) and diffraction-enhanced image (bottom) of breast specimen.

E.D. Pisano, R.E. Johnston, D. Chapman, J. Geradts, M.V. Iacocca, C.A. Livasy, D.B. Washburn, D.E. Sayers, Z. Zhong, M.Z. Kiss, and W.C. Thomlinson, "Human breast cancer specimens: Diffraction-enhanced imaging with histologic correlation—Improved conspicuity of lesion detail compared with digital radiography," *Radiology* **214**, 895 (2000).

In conventional mammograms, differences in tissue densities and composition show up as contrasting areas due to x-ray absorption, allowing doctors to see tumors or changes in tissue. However, differences between healthy and cancerous tissues are very small, and scattering of x-rays can lead to blurring and even lower contrast. Researchers have developed a new mammography technique called diffraction-enhanced imaging (DEI) that uses ultrabright x-rays and provides a dramatic contrast between normal tissues and tumors. The DEI method uses a single-energy beam of x-rays instead of the broad-energy beam used in conventional imaging. The key to the new imaging method is an analyzer crystal placed between the tissue under study and the x-ray detector. The analyzer can differentiate between x-rays that are traveling much less than one ten-thousandth of a degree apart. This method of line-scan imaging reduces scatter and helps visualize low-contrast areas that otherwise would be lost. This technology offers great hope for early detection of breast cancer and therefore allows for higher survival percentages. DEI could be used in experimental clinical trials within five years and possibly in routine mammography in ten years. In addition to mammography, potential applications of DEI include other low-contrast tissues and organs such as kidneys, and the nondestructive testing of materials.

## X-Ray Imaging of Shock Waves Generated by High-Pressure Fuel Sprays



Time-resolved radiographic images of fuel sprays and attendant shock waves.

A.G. MacPhee, M.W. Tate, C.F. Powell, Y. Yue, M.J. Renzi, A. Ercan, S. Narayanan, E. Fontes, J. Walther, J. Schaller, S.M. Gruner, and J. Wang, "X-ray imaging of shock waves generated by high-pressure fuel sprays," *Science* **295**, 1261 (2002).

High-pressure, high-speed fuel sprays are a critical technology for many applications, including fuel injection systems, where the structure and dynamics of the fuel sprays are the key to increasing fuel efficiency and reducing pollutants. But because liquid sprays are difficult to image, particularly in the region close to the nozzle, high-pressure fuel sprays have never been considered as supersonic under typical fuel injection conditions. Synchrotron x-ray radiography and a fast x-ray detector were used to record the time evolution of transient fuel sprays from a high-pressure injector, capturing the propagation of spray-induced shock waves in a gaseous medium and revealing the complex nature of the spray hydrodynamics. The x-ray radiographs also allow quantitative analysis of the shock waves that would be nearly impossible with optical imaging. Under injection conditions similar to those found in operating engines, the fuel jets can exceed supersonic speeds and result in gaseous shock waves. This work sets the stage for study of the entire range of fluid dynamics inside and close to high-pressure liquid sprays. The methods used here may also be applied to the characterization of highly transient phenomena in optically dense materials.

## 10: SOFT X-RAY IMAGING

**OTHER DESIGNATIONS:** Soft x-ray imaging, photoelectron emission microscopy (PEEM), scanning transmission x-ray microscopy (STXM), full-field microscopy, x-ray diffraction imaging (XDI), x-ray tomography, computer-aided tomography (CAT) scans.

**PURPOSE:** The wavelengths of soft x-ray photons (1–15 nm) are very well matched to the creation of nanoscopes capable of probing the interior structure of biological cells and inorganic mesoscopic systems. Problems addressed by soft x-ray imaging techniques include:

- Cell biology
- Nanomagnetism
- Environmental science
- Soft matter, polymers

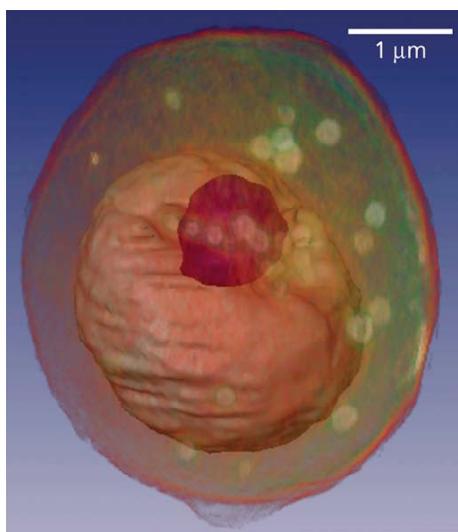
**HOW THE TECHNIQUE WORKS:** The fine spatial resolution needed in soft x-ray microscopy can be attained by use of photon optics or electron optics.

- (1) Photon optics. Fresnel zone plates perform the same function for x-rays that lenses do for visible light. With STXM, the sample is scanned through the illuminated spot to build up an image. With the use of two zone plates (a condenser and an objective), it is possible to create a full-field image.
- (2) Electron optics. In PEEM, a smallish spot on the sample is illuminated and the emitted photoelectrons are passed through an electron microscope column to produce a magnified full-field image.

**UNIQUENESS:** The tunability of synchrotron radiation is absolutely essential for the creation of contrast mechanisms. Cell biology CAT scans are performed in the “water window” (300–500 eV). Nanomagnetism studies require the energy range characteristic of iron, cobalt, and nickel (600–900 eV).

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### CAT Scans of Single Cells Show Details Invisible to Light Microscopy

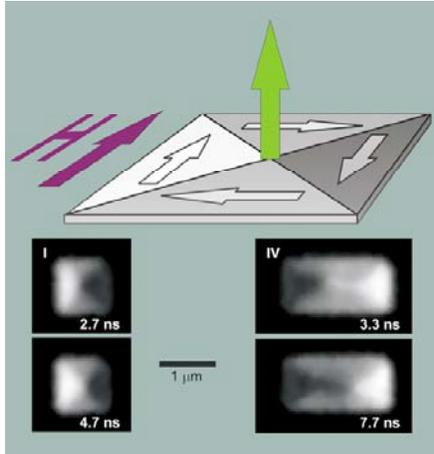


Tomographic reconstruction of *Saccharomyces cerevisiae* (yeast).

C.A. Larabell and M.A. Le Gros, “X-ray tomography generates 3-D reconstructions of the yeast, *Saccharomyces cerevisiae*, at 60-nm resolution,” *Molecular Biology of the Cell* **15**, 957 (2004).

X-ray tomography is the first high-throughput imaging technology that generates images of whole, hydrated cells at better than 60-nanometer resolution. With it, researchers have obtained three-dimensional views of the internal structure of whole, hydrated *Saccharomyces cerevisiae* (yeast) cells, bridging the mesoscale resolution “gap” — the middle area between light (200 nm) and electron microscopy (3 Å). With the ALS transmission x-ray microscope, data collection is fast (under 3 minutes) and relatively easy (like light microscopy), producing high-resolution, absorption-based images (like electron microscopy) that provide contrast between cellular structures and allow for discernment of individual structures. After data collection, tomographic techniques are used to reconstruct the original information into quantifiable three-dimensional views of the entire cell. Through the use of computer algorithms, the researchers then process the reconstructed data to create made-to-order images of whole cells and their internal structures.

## Nanomagnetism Dynamics

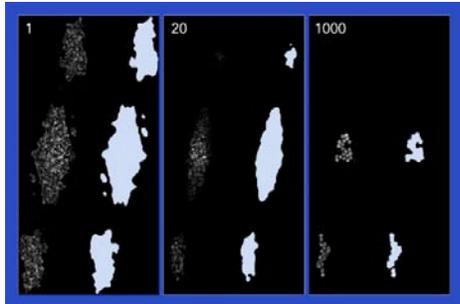


*Time-resolved PEEM images of square and rectangular vortex patterns.*

S.-B. Choe, Y. Acremann, A. Scholl, A. Bauer, A. Doran, J. Stöhr, and H.A. Padmore, "Vortex-driven magnetization dynamics," *Science* **304**, 420 (2004).

Any desktop or laptop computer user knows how fast the storage capacity of hard disks is growing. To maintain this pace, we require new tools to study magnetic materials in smaller areas and over shorter times. Researchers have used a new time-resolved x-ray photoemission imaging technique to resolve the motion of magnetic vortices, peculiar magnetic structures that appear in micron-size magnetic patterns in response to an excitation field pulse. They are of considerable technological interest because a low stray magnetic field leads to a magnetic stability and minimizes the cross-talk between adjacent vortices—two prerequisites for high storage densities. For the microscopic study of such ultrafast magnetization dynamics, researchers developed a novel technique based on 70-picosecond-long synchrotron x-ray pulses that can be used like light flashes from a strobe to freeze the dynamics and acquire a snapshot of the motion. Analysis of the observed gyrating trajectory of the core on such short time scales suggests that the precession is induced by a left-right handedness, or chirality, in the magnetization pattern, thereby demonstrating that handedness plays an important role in the dynamics of microscopic magnets.

## Imaging Without a Lens



*Image reconstruction of two clusters of gold balls showing convergence of both the reconstructed image (on the left of each panel) and its boundary (on the right of each panel) as the number of iterations increases from 1 to 1000.*

S. Marchesini, H. He, H.N. Chapman, S.P. Hau-Riege, A. Noy, M.R. Howells, U. Weierstall, and J.C.H. Spence, "X-ray image reconstruction from a diffraction pattern alone," *Phys. Rev. B* **68**, 140101(R) (2003).

For samples consisting of a very large number of identical objects in a regular array (e.g., atoms in a crystal), it is mathematically possible to construct an image of the object from its diffraction pattern. Researchers are now taking image reconstruction a big step further by studying nonperiodic samples using x-ray diffraction imaging (XDI), or "lensless imaging." Like crystallography, XDI is based on the analysis of diffraction patterns, but it uses iterative algorithms to extract the phase information needed to reconstruct the object and requires that the diffraction intensity be zero outside the object's boundary. The better this boundary is known, the faster the iterations converge to an accurate image. Most researchers have relied on x-ray microscopy or other techniques to supply this information. Now, researchers have done away with this requirement through the use of a new "shrink-wrap" algorithm, which uses a transform of the diffraction pattern itself to provide initial information about the boundary. The technique has demonstrated the ability to make two-dimensional images of clusters of gold balls 50 nm in diameter. The researchers anticipate that a three-dimensional resolution of 10 nm will be possible for life-science samples, where radiation damage is an issue, and 2 nm for solids.

## 11: INFRARED IMAGING

**OTHER DESIGNATIONS:** Infrared (IR), microspectroscopy, infrared imaging, infrared microprobe.

**PURPOSE:** Mid- and far-infrared (energies below 1 eV) microprobes using synchrotron radiation are being used to address problems such as:

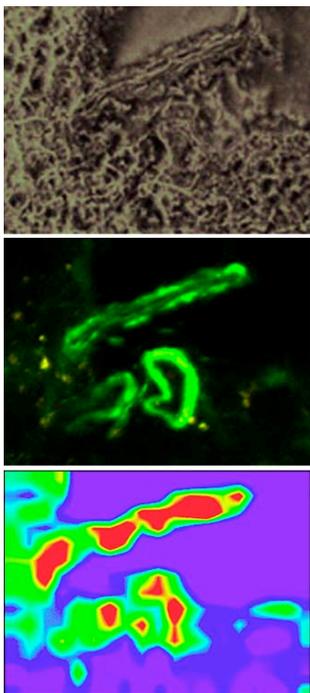
- Chemistry in biological tissues
- Chemical identification and molecular conformation
- Environmental biodegradation
- Mineral phases in geological and astronomical specimens
- Electronic properties of novel materials
- Forensic studies

**HOW THE TECHNIQUE WORKS:** Infrared synchrotron radiation is focused through, or reflected from, a small spot on the specimen and then analyzed using a spectrometer. Tuning to characteristic vibrational frequencies serves as a sensitive fingerprint for molecular species. Images of the various species are built up by raster scanning the specimen through the small illuminated spot.

**UNIQUENESS:** Infrared radiation from a synchrotron is more intense than that from a conventional laboratory source. Even so, the radiation dose is mild and nondestructive, permitting the study of fragile specimens and even live biological systems.

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### Misfolded Protein Structure in Alzheimer's Disease

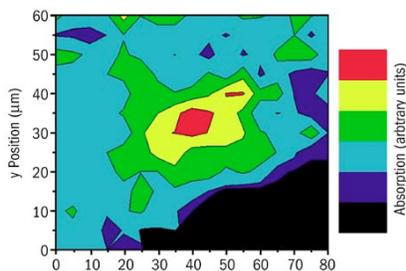


Visible-light, UV, and IR images of Alzheimer's diseased brain tissue.

Alzheimer's disease is characterized by the death of nerve cells in particular regions of the brain. The brain shrinks as gaps develop in the temporal lobe and hippocampus, which are responsible for storing and retrieving new information. This in turn affects a patient's ability to remember, speak, think, and make decisions. It is not known what causes nerve cells to die but there are characteristic appearances of the brain after death. In particular, "tangles" and "plaques" made from protein fragments are observed under the microscope in damaged areas of brain. A combination of ultraviolet and infrared light is being used to study the structure of the proteins involved in the formation of plaques and tangles in the brain. Fluorescence microscopy is used to identify the plaques and tangles, and infrared imaging is used to determine their structures within brain tissue. At the same time, infrared imaging is also used to study the health of the nerve cells surrounding the plaques and tangles in the brain tissue. Understanding the structures of the plaques and tangles in Alzheimer's-diseased brain tissue may help to develop ways of preventing them from forming, thus preventing progression of the disease. In addition, identification of plaques and tangles in other organs may provide a biopsy method for early diagnosis of Alzheimer's disease in the future.

L.M. Miller, P. Dumas, N. Jamin, J.-L. Teillaud, J. Miklossy, and L. Forro, "Combining IR spectroscopy with fluorescence imaging in a single microscope: Biomedical applications using a synchrotron infrared source," *Rev. Sci. Instr.* **73**, 1357 (2002).

## Biodegradation of Organic Contaminants Catalyzed by Humic Acid

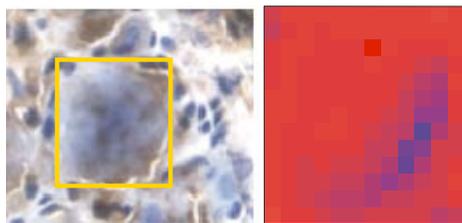


Contour diagram from infrared mapping showing the distribution of *Mycobacterium sp. JLS* bacteria on a mineral surface.

H.-Y Holman, K. Nieman, D.L. Sorensen, C.D. Miller, M.C. Martin, T. Borch, W.R. McKinney, and R.C. Sims, "Catalysis of PAH biodegradation by humic acid shown in synchrotron infrared studies," *Environ. Sci. Technol.* **36**, 1276 (2002).

Contaminants in the environment come in many forms, one of which is that of the toxic organic (carbon-based) chemicals known as polycyclic aromatic hydrocarbons (PAHs). These include more than 100 different chemicals resulting from incomplete burning of coal, oil, gas, garbage, and other organic substances like tobacco or grilled meat. Converting PAHs into nontoxic chemicals removes the hazard, but learning how to do this in an efficient and cost-effective way remains to be accomplished. Remarkably, since bacteria are feared by many people as infectious germs, some species of these microorganisms may provide a solution by, in effect, ingesting the PAHs and during digestion converting them into a less toxic chemical, a process known as biodegradation. Researchers have made use of an infrared technique to show that the speed of biodegradation can be dramatically increased (almost a hundred times) by adding a soil-derived organic (humic) acid along with the bacteria to a PAH spot on a mineral surface. This finding will influence the development of environmental cleanup strategies based on biodegradation.

## In Situ Prion Protein Structural Changes in Mad Cow Disease and Scrapie



Left: Light microscope image of an immunostained prion-infected cell. Right: Infrared image of the Amide I absorption maximum, which shows the misfolded prion protein located in or near the cell membrane of the infected cell.

J. Kneipp, L.M. Miller, M. Joncic, M. Kittel, P. Lasch, M. Beekes, and D. Naumann, "In situ identification of protein structural changes in prion-infected tissue," *Biochim. Biophys. Acta.* **1639**, 152 (2003).

Transmissible spongiform encephalopathies, such as scrapie, mad cow disease, and Creutzfeldt-Jakob disease, are a group of fatal neurodegenerative disorders characterized by the conversion of the normal prion protein (PrP) into misfolded aggregates (PrP<sup>Sc</sup>). The mechanism behind this structural conversion is unclear. To analyze the disease-related protein structural changes directly in the tissue environment, scientists have examined the protein structure within the dorsal root ganglia in scrapie-infected Syrian hamsters. Using synchrotron-based infrared microscopic imaging, individual neurons are scanned for the distribution of protein structure based on the infrared absorption of the protein backbone mode. The high brilliance of the synchrotron infrared light source permitted subcellular spatial resolution. The scientists observed regions of increased structural change in and/or around scrapie-affected cells. No evidence of these structural changes is observed in normal neurons. Comparison of the infrared images with PrP<sup>Sc</sup> immunostaining of the same tissue demonstrated that the altered regions correspond to the misfolded structure of PrP<sup>Sc</sup>.

## 12: LITHOGRAPHY

**OTHER DESIGNATIONS:** Extreme ultraviolet (EUV) lithography, interferometry, LIGA (lithographie, galvanofornung und abformung — translation: lithography, electroplating and molding), microelectromechanical structures (MEMS).

**PURPOSE:**

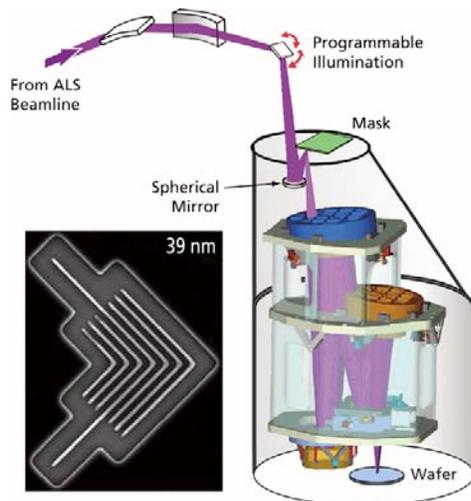
- (1) Explore whether the demagnifying mirrors needed in EUV lithography, a candidate for the next technology in the production of microchips, can be manufactured to the desired specifications.
- (2) Explore and implement the manufacture of microscale mechanical components using LIGA or MEMS.

**HOW THE TECHNIQUE WORKS:** Lithography, a technique used in the art world for many centuries, has been adopted and adapted with phenomenal success by the high-tech industry. In microchip manufacturing, a silicon wafer is coated with a thin layer of photosensitive material called a resist. An image of a mask containing the desired pattern is projected onto the resist. The exposed (or unexposed) parts of the resist are etched away and, with further processing, the desired circuit is built up. The same basic process can be used in the manufacture of small mechanical components. Work at synchrotron light sources focuses primarily on the exposures of the resists.

**UNIQUENESS:**

- (1) The high coherence of synchrotron radiation is absolutely essential for mirror interferometry.
- (2) High flux and favorable spectral range are essential for short exposure times in LIGA/MEMS.

### EUV Lithography, the Next Microchip Manufacturing Technology



*A mirror directs focused EUV light into an interferometer. By controlling the exposure, researchers were able to print line widths down to 39 nm for an elbow test pattern with a line-to-spacing ratio of 3:1.*

P.P. Naulleau et al., "Static microfield printing at the Advanced Light Source with the ETS Set-2 optic," *Proc. SPIE* **4688**, 64 (2002).

In conformance with Intel co-founder Gordon Moore's 1965 prediction, now known as "Moore's Law," the density of circuit elements on microchips has doubled roughly every 18 months for more than 30 years, resulting in ever smaller, faster, and cheaper computers. However, the traditional technique for printing circuit patterns — optical lithography based on refractive optics (lenses) — cannot continue indefinitely on this course. Today's leading candidate for a successor, known as extreme ultraviolet (EUV) lithography, relies on reflective optics (mirrors). With wavelengths 50 times smaller than those of visible light, EUV techniques will be able to draw circuit patterns just tens of nanometers wide. Before that day arrives, however, there is the matter of producing accurate EUV lithography cameras. As an old adage says, "If you can't measure it, you can't make it." EUV metrology beamlines have been instrumental in a five-year, \$250-million industry effort to bring EUV lithography to the commercial stage. The first printing results reveal the extraordinarily high quality of the lithography optics and demonstrate the importance of EUV metrology beamlines in helping to achieve the very tight specifications for figure, finish, and multilayer coatings required of the mirrors comprising the lithography optics. By printing actual test patterns with ultrathin line widths, researchers have verified that the optics fabricated for a prototype camera are indeed on the path to the required performance.

### Rotary Millimotor

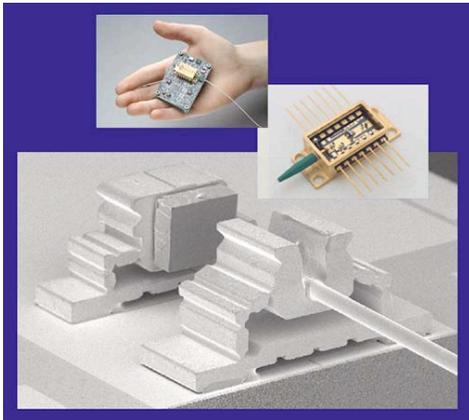


*LIGA-micromachined gear for a miniature electromagnetic motor.*

*Link: [www.ca.sandia.gov/liga](http://www.ca.sandia.gov/liga).*

By using the penetrating power of x-rays from a synchrotron, LIGA allows the fabrication of structures which have vertical dimensions from hundreds of microns to millimeters and horizontal dimensions which can be as small as microns. These are three-dimensional microstructures defined by two-dimensional lithographic patterns. The height-to-width ratio capability is relevant to the manufacturing of miniature components that can withstand high pressure and temperature, and can transfer useful forces or torques. The feature definition, radius, and side wall texture using LIGA are superior to current precision machining techniques. A miniature electromagnetic motor that fits in a volume 8 millimeters in diameter by 3 millimeters in height has been designed, fabricated, and tested. The torque goal for this millimotor was greater than 1.5 milli Newton-meters. The millimotor has been tested at speeds up to 1600 rpm, well below the maximum currents that coils are expected to withstand. Further tests to measure torque are planned.

### Commercial LIGA Microfabrication for Optoelectronics



*AXSUN uses the LIGA process to create a new packaging platform for photonics using micro-optic lens and micro-alignment technology.*

*Link: [www.ligafoundry.com](http://www.ligafoundry.com).*

Originally developed in Europe, LIGA has only recently been accepted as a proven, commercially available production process. Today, millions of high-precision parts are fabricated using LIGA production processes. A commercial LIGA beamline has been established by AXSUN Technologies, a Massachusetts-based company that provides miniaturized optoelectronic modules for fiber-optic telecommunications networks. These modules are essentially optical benches the size of computer chips, containing complex assemblies of high-precision optical, mechanical, and electrical subassemblies that align and focus incoming photon signals, convert them into electrical signals, and route them through switches into the appropriate paths. AXSUN uses LIGA techniques at the new beamline for the microfabrication of key alignment structures (patent pending) measuring roughly 2 millimeters wide by 500 micrometers thick.