MATERIAL PROPERTIES

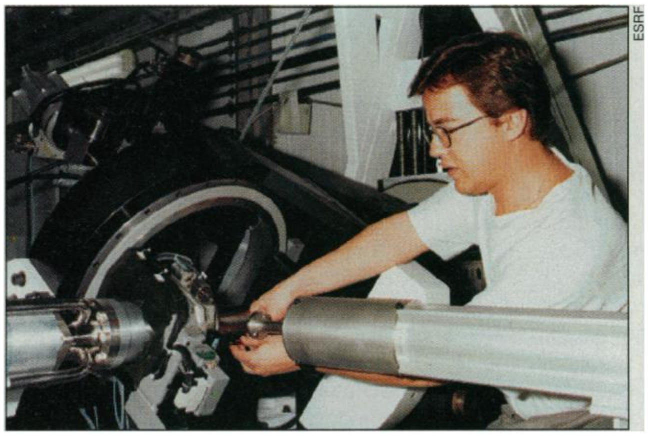
X-rays Go Where Neutrons Fear to Tread

Move over, neutrons: The x-rays are in town. Ever since the German physicist Max von Laue's 1913 insight that x-rays could be used to unravel crystal structure, they have been an essential tool for the study of matter. Some neighborhoods, however, have been off limits to x-rays, such as materials' fine-scale magnetic structure and the fleeting molecular alliances within disordered materials such as liquids and glasses. Those have been the domains of neutron beams since the first research reactors were built in the 1950s. With the advent of third-generation synchrotron sources, however, x-ray scattering is making inroads into neutron territory.

"The special points [of the new sources] are very high brightness, good-quality polarization, and very high energy x-rays," says Hiroshi Kawata of the Photon Factory at the KEK high-energy physics lab in Tokyo. Because of these properties, "you can start thinking about experiments it would not have been possible to do a few years before," says physicist Michael Krisch of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, the first of the new machines. Already, the third-generation sources are teasing out information about magnetic properties and disordered materials that neutrons could not reveal. Because of the beams' exquisite polarization, says ESRF's Pekka Suortti, researchers are beginning to answer such questions as "What is the real nature of the magnetization: Is it local [to an atom] or is it itinerant?" And the x-rays' brightness and tightly controlled energy have opened the way to studies of disordered materials that capture, for example, a high-speed form of sound in water.

Those results are only the first in what is expected to be a torrent, says David Laundy, an ESRF user from Britain's University of Warwick, because "x-rays give different information from [that of] neutrons." Neutrons are sensitive to magnetism, for example, because they are scattered not only by collisions with atomic nuclei, but also by magnetic interactions with atoms as a whole. (Neutrons, although they lack charge, nevertheless have their own magnetic field.) But neutrons cannot distinguish the two contributions to an atom's magnetic field, which come from the inherent spin of its electrons and from the magnetic effect of those electrons orbiting the nucleus. "In the case of neutrons ... you see the combined magnetic effect, which includes both the spin and orbital contributions," says Suortti. Separating out the spin and orbital parts "really lies at the heart of understanding magnetic properties," he says, because while the orbital component is always associated with the atom, the spin component can become "delocalized" and give rise to a "sea" of magnetism like that in metals such as iron.

X-rays offer a way to untangle these two effects. Scattered by an atom's electrons, x-rays respond mainly to the electrons' electric charge, but the magnetic part of the photon's electromagnetic wave also interacts feebly with the electrons' magnetic field if they are aligned advantageously. This is possible with the new x-ray sources, because they have beams whose polarization—the alignment of their electric and magnetic fields—can be controlled. "With x-rays ... magnetic and charge-scattering amplitudes have a different polarization dependence," explains ESRF's Christian Vettier. "If we measure this, we can tell whether the scattering is magnetic in origin or not." With a weak x-ray beam, this magnetic scattering is little more than a curiosity, but with a bright beam, it can become a tool for studying magnetic structure.



New attractions. Intense x-ray beams have allowed researchers at ESRF to build a magnetic scattering beamline, shown above.

And it turns out that x-rays are also sensitive to the two different components of magnetism. "If you do two different experiments in two different geometries," with the sample in different orientations relative to the incoming x-rays, "you get different proportions of spin scattering to orbital scattering," says Laundy. In short, adds Suortti, "By [using] x-rays, you can separate the orbital and spin contributions."

X-rays offer other advantages over neutrons. "X-rays don't penetrate very far into materials compared to neutrons, so they tend to be more sensitive to the surface of the material than neutrons," according to Laundy, who adds that surface magnetism is of great interest in the world of magnetic recording devices. Laundy also sees a future for x-rays in studying exotic magnetic structures—for example, those in which the orientation of the magnetism spirals inside the material. "X-rays offer high resolution compared to neutrons for studying these materials," he says.

X-rays are also flexing their muscles in another domain that was once the preserve of neutrons—so-called inelastic scattering. Most structural studies carried out with neutrons and x-rays rely on elastic scattering, in which the scattering does not change the energy of the probe particle. Such studies yield a still image of the inner material world. Probing the dynamics of that world requires inelastic scattering, in which the probe particle provokes an excitation, such as a lattice vibration, as it strikes the sample, then continues on its way with reduced energy. Careful analysis of the energy and momentum of the particle before and after scattering allows researchers to find out what sort of excitations are possible in the material.

Inelastic scattering studies with neutrons have unraveled the dynamics of a wide range of systems, from liquids to metallic glasses. But neutron studies often require samples to be made from rare isotopes, rather than the common ones. Water, for example, has to contain deuterium rather than hydrogen for neutron studies. Neutron beams are also dim, and their energy range is limited. And, like police who can't catch up with villains in sports cars, neutrons can't trace excitations that propagate faster than about 1000 meters per second, roughly the speed of the neutron itself.

ESRF's x-rays, however, have a wide range of energies and momenta, enabling Francesco Sette and his colleagues to study just this type of fast excitation process. "We are interested in determining the dynamical properties of disordered materials in a region that was not accessible before," says Sette, who has a special interest in liquids. At large scales, liquids are shifting and chaotic; at the smallest scales they consist of individual particles. Somewhere in between, liquid molecules interact fleetingly with their neighbors, arranging themselves into structures that are gone again in a flash. For brief moments, the water may even appear to be a solid. These transitory get-togethers by molecules are called collective excitations, and they may affect everyday properties of a liquid, such as chemical reactions, thermal properties, and the way sound waves propagate.

Collective excitations are also thought to be responsible for the phenomenon of "fast sound" in water. Sound usually travels at about 1400 meters per second in water, but about 4000 meters per second in ice. Computer simulations predict that collective excitations in water allow a second, faster form of sound to travel at 3200 meters per second. Paris-based physicist José Teixeira and his colleagues first glimpsed fast sound in 1985 using neutron scattering, although further neutron studies a decade later cast doubt on their findings.

However, Sette and colleagues from ESRF and from the University of L'Aquila in Italy confirmed the effect by setting off fast sound waves in water with inelastically scattered x-rays. "We were able to show that you can have in a liquid a transition to properties characteristic of the solid when you consider time and length scales which are short and small [enough]," says Sette, who reported the result in the 1 July 1996 issue of *Physical Review Letters*.

Solid but disordered materials such as glass are also coming under the gaze of inelastic x-ray scattering. Glass is remarkably good at absorbing heat, for example, and Sette led scattering experiments at ESRF showing that some of this ability "must come from high-frequency acoustic waves." He notes that he and his colleagues "were able to observe and to measure and to characterize [these waves] in a glass, and this was not possible before."

Despite their newfound abilities, x-rays are not about to replace neutrons as a tool for studying matter. Laundy describes the two as complementary, a sentiment echoed by Sette. When it is possible to use them, "neutrons are by far ... the best technique to look at the dynamics," he says. And even though x-rays can probe magnetism in ways neutrons cannot in many situations, "neutrons are still the probe of choice to determine a magnetic structure," says Vettier, because their magnetic scattering is so much stronger. But researchers at the new synchrotron sources are learning fast, and x-rays may not remain the underdog for long.

–Andrew Watson

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BIOLOGY

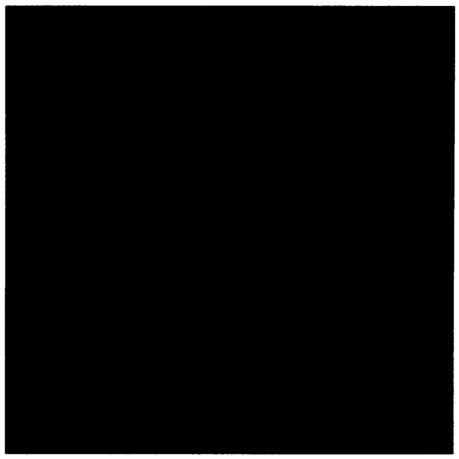
Brightness Speeds Search for Structures Great and Small

To Eva Pebay-Peyroula and other x-ray crystallographers, bacteriorhodopsin has brought 20 years of frustration. Beginning in the mid-1970s, researchers managed to coax this large protein (which helps convert sunlight to chemical energy in bacteria) into crystals, the starting point for x-ray experiments that they hoped would determine the protein's three-dimensional (3D) atomic structure and reveal how it does its job. But while other experiments have unraveled a good deal of the molecule's structure, the x-ray studies never panned out. The crystals were either too small or too disorderly to be useful, making the atomic pictures come out fuzzy at best.

Last winter, however, Pebay-Peyroula, a crystallographer at the University of Grenoble in France, finally triumphed over the elusive protein. Together with crystal growers Ehud Landau and Jurg Rosenbusch of the University of Basel in Switzerland, Pebay-Peyroula took a newly grown batch of pinhead-sized crystals—no bigger than the ones that had failed in earlier studies—to a new ultrafine x-ray beam at the European Synchrotron Radiation Facility (ESRF) in Grenoble. They walked away with the first high-resolution x-ray picture of the molecule, the details of which she presented at last month's European Biophysics Congress in Orleans, France. The new structure not only reveals new aspects of how the water molecules at the core of bacteriorhodopsin help pump protons across cell membranes to help generate chemical energy; it also highlights the new frontier of molecular biology being made possible at the latest generation of synchrotrons. "It's a really big success that could only have been done on this beamline," says Stephen Cusack, a crystallographer at the European Molecular Biology Laboratory's facility in Grenoble.

ESRF, which has been up and running since 1994, is one of three so-called "third-generation" synchrotron sources that turn out highly energetic, or hard, x-rays; the other two are just starting operations in the United States and Japan. The main advantage of these stadium-sized machines, which generate radiation by accelerating charged particles to high energies and sending them along tightly curving paths, is that "their beams are fantastically bright compared with other sources," says Wayne Hendrickson, a biochemist at Columbia University in New York City. They are at least 100 times as bright, in fact, thanks to the high energies of the particles, as well as the addition of specialized instruments designed to enhance and focus the beams. That puts them "head and shoulders above other machines," says Edwin Westbrook, a crystallographer who heads a structural biology collaboration at the Advanced Photon Source (APS), the United States' third-generation synchrotron, which officially opened for business in May 1996.

That brightness, according to Westbrook, Hendrickson, and others, will allow researchers to study biomolecules as never before. For the first time, the ultrasmall crystals of proteins such as bacteriorhodopsin are yielding enough data for researchers to determine their structures. The intense beams are lighting up the atomic landscapes of protein complexes, such as viruses, that are too large to be studied with fainter beams. They are speeding discoveries by turning out, in just seconds, the amount of data that previous machines required minutes or hours to amass. That speed is also helping researchers make high-speed movies of proteins as they undergo shape changes (*Science*, 27 June, p. 1986). Moreover, because the beams are so bright, they can reveal details hidden in partially ordered samples, such as the molecular events responsible for muscle contractions.



A. HOWARD/IIT

Connect the dots. Spots produced by a beam of x-rays diffracted from a protein crystal.

Starting small. While synchrotrons got their start as scientific toys for physicists, chemists, and materials researchers, today biologists make up the fastest growing set of users, up from 5% just 10 years ago to 30% today. The reason: The machines' hair-thin x-ray beams are ideal for determining the 3D structure of proteins. While such structures can be deter-