

Femtosecond snapshots capture atomic motion in a powdered solid

A new technique sets the stage for ultrafast diffraction studies of materials that can't easily be crystallized.

X-ray diffraction has long been an important tool for deducing crystal structures. The x rays scatter off the crystal's electrons, giving a pattern of diffraction peaks related to the electron density; points of concentrated electron density indicate the nuclear positions. In recent decades time-resolved x-ray diffraction has probed faster and faster structural changes, up to and including atomic movements on the femtosecond time scale.

Until now, the fastest time-resolved experiments have used samples in the form of single crystals. But many materials of interest, such as the transition-metal complexes used in organic photovoltaic cells, can't readily be made into crystals of sufficient size and quality.

Michael Woerner, Thomas Elsaesser, and colleagues at the Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy in Berlin have now demonstrated femtosecond x-ray powder diffraction, in which the sample is a collection of randomly arranged microcrystals, and the diffraction pattern is a set of concentric rings rather than discrete peaks.¹⁻³ The team's advance was in engineering its x-ray source, which converts an ultrafast optical laser pulse into an equally brief x-ray pulse, to run at high repetition rate for many hours at a stretch.⁴

The researchers tested their system on powdered ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, following ultrafast photoexcitation at 400 nm. They observed a never-before-seen concerted motion, in which a proton broke away from an NH_4^+ ion, briefly met up with an electron escaped from an SO_4^{2-} ion, and then returned to its original position. Surprisingly, that fleeting structural change bears no resemblance to any of ammonium sulfate's known phase transitions.

Taking a powder

X rays scattering off a crystal's periodic lattice planes interfere constructively and produce a diffraction peak whenever the Bragg condition is met:

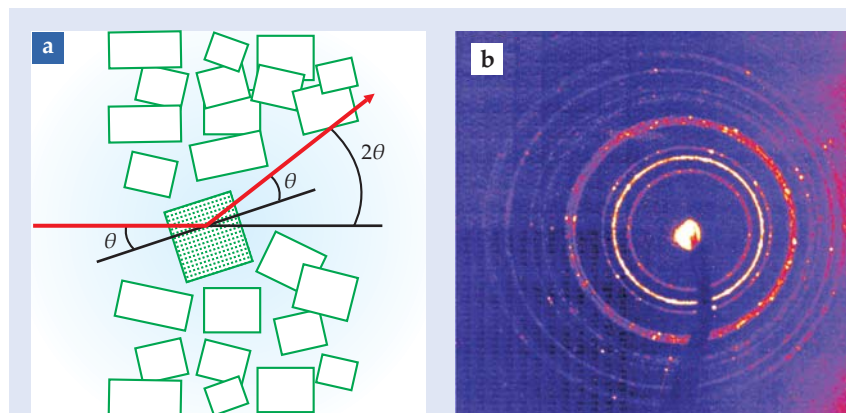


Figure 1. (a) In x-ray powder diffraction, an x-ray beam (red) scatters constructively off a randomly oriented microcrystal whenever the crystal's orientation satisfies the Bragg condition. **(b)** The result is a diffraction pattern of concentric rings, each one comprising a different Bragg peak. Bright spots within the rings result from larger-than-average powder grains. (Adapted from ref. 2.)

$n\lambda = 2d\sin\theta$, where n is any integer, λ is the x-ray wavelength, d is the distance between lattice planes, and θ is the angle between the planes and the x-ray beam. (The peak's intensity is related to the Fourier transform of the electron density.) When the sample is a single crystal and the x rays are monochromatic, only a few sets of lattice planes satisfy the Bragg condition at any one time. Solving the crystal structure requires several diffraction images at different orientations, each with the crystal precisely aligned with the x-ray beam. Time-resolved single-crystal studies often focus on one or a few Bragg peaks, from which one can infer key aspects of the structural change.

In powder diffraction, on the other hand, some portion of the sample is sure to satisfy the Bragg condition for every lattice plane, as shown in figure 1a. Each lattice plane generates a ring with angular radius 2θ , as shown in figure 1b. It's more difficult, but not impossible, to solve an unknown crystal structure from a powder diffraction pattern than from a single-crystal study. But powder diffraction has long been used to identify substances from among a catalog of known structures. And it

has the potential to be useful for detailed time-resolved studies, since the intensity change of every ring can be measured simultaneously.

Laser driven

Early time-resolved x-ray studies investigated slow changes, such as melting transitions. Faster studies usually look at a sample's response to an optical excitation. Their time resolution depends both on the degree of synchronization between the optical pump pulse and the x-ray probe and on the duration of the pulses themselves.

Synchrotrons can produce x-ray pulses tens to hundreds of picoseconds in duration. (See PHYSICS TODAY, March 2001, page 19.) And there exist schemes for extracting 100-fs slices from synchrotron pulses, which can then be synchronized with a femtosecond pulsed laser. Free-electron lasers, such as the Linac Coherent Light Source (LCLS) at SLAC, are also starting to produce bright femtosecond x-ray pulses. (See PHYSICS TODAY, August 2009, page 21.) But synchrotrons and FELs are large, shared, and often distant facilities; beam time at them is limited.

The Berlin researchers produced

every unit cell was excited.

Knowing that only a small fraction of their sample was excited, the researchers used a clever trick to reconstruct the transient electron density. They wrote down an expression for the transient diffraction ring intensities in terms of the interference between a majority of unexcited units and a minority of excited units, and they discarded all the terms that were higher than first order in the fraction of excited units. That approximation quickly led them to an expression for the change in electron density in reciprocal space in terms of the change in ring intensity.

Converting from reciprocal space into real space gave a three-dimensional time-dependent charge-density map. A 2D cross section is shown in figure 3: The first panel shows the equilibrium structure (only oxygen atoms are present in this slice through the crystal structure), and subsequent panels show the changes in electron density in response to excitation. The red blobs across the middle show that electron density is pooling in a place where no nucleus exists in the equilibrium structure. Because the density is localized, there must be an accompanying nucleus—namely a proton—that migrates to that spot. By stipulating that the blob of electron density represent exactly one electron, the researchers determined that 6% of the unit cells were excited. Although the electron density appears to be coming from the oxygen atoms, most of it actually comes from the sulfur atoms, not shown.

“We were totally surprised,” says Elsaesser, to see a structural change so different from any known phase transition of ammonium sulfate. Two such transi-

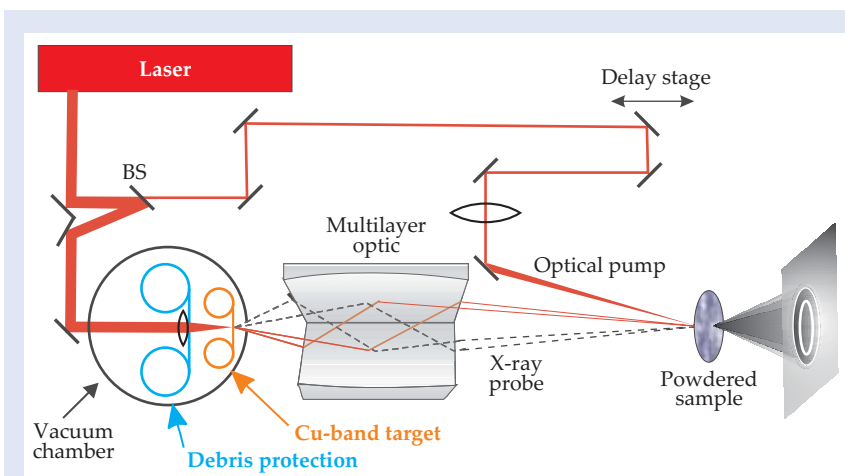


Figure 2. Laser-driven plasma x-ray source for ultrafast powder diffraction. The optical pump and x-ray probe pulses are derived from the same laser beam via a beamsplitter (BS). Most of the beam enters a vacuum chamber, where it is focused onto a thin copper tape and generates x rays. (Adapted from ref. 2.)

their femtosecond x-ray pulses in their own lab, using a source like the one sketched in figure 2. Light from a commercial pulsed optical laser is focused tightly onto a micron-thin copper target. First, the laser beam ionizes the copper and dislodges ions, generating a plasma over the surface of the target. Then the beam’s electric field accelerates the plasma electrons so that they smash back into the copper target with enough energy to knock out some core electrons. Higher-energy electrons tumble down to take the core electrons’ places. The hard (8-keV) x rays thus emitted are collected with x-ray optics, and focused onto the sample.

The plasma electrons are accelerated only when the laser field is present, so the x-ray pulse is just as short as the laser pulse. And when the optical pump and x-ray probe pulses are derived from the same laser, their timing can easily be controlled with a delay line.

Plasma x-ray sources using a variety of target metals have been used since the early 1990s.⁵ But for most of that time, their repetition rate, and therefore their total x-ray flux, has been limited. One shot of the laser beam irreversibly damages the target surface, which needs to be refreshed before the next pulse arrives. If the laser is to run at 1 kHz, the target needs to be kept moving at about 4 cm/s. And to keep the tight focus of the laser beam on the surface, the target can’t wobble by more than a few microns.

Elsaesser, Woerner, and colleagues designed a system in which the target is a long copper tape wound off one spool and onto another. A parallel plastic tape collects the debris from the plasma. When the laser beam has “written” a

track along the length of the copper, the spools automatically shift and reverse direction. With one copper tape, the system can operate at 1 kHz for about 15 hours.

Electron dance

Compared with ammonium sulfate’s equilibrium diffraction pattern, measured with the optical pump turned off, the rings in the time-resolved pattern changed in intensity but not location. That means the size and shape of the unit cells didn’t change, but the structures within them did. Or rather, the structures within some of them did: The powder sample, 250 μm thick, is a strong scatterer at optical frequencies, so the pump pulse penetrated only about 1/10 of the way through it. And even in the penetration region, not

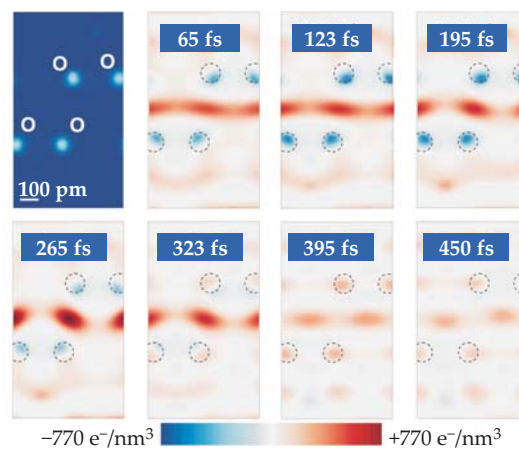


Figure 3. Time-resolved electron density shown for one cut through an ammonium sulfate crystal. The first panel shows the equilibrium structure: Dark blue indicates low density, and the white spots indicate regions of concentrated electron density surrounding oxygen nuclei. The remaining seven panels show the change in electron density in response to excitation by the optical pump. The localized red spots along the center of the

images—where there are no nuclei in the equilibrium structure—mean that hydrogen nuclei have migrated to those locations. (Adapted from ref. 1.)

tions are known—one at 223 K involving a change in symmetry and one at 423 K involving a change in unit-cell size—and although the experimenters took care not to heat or cool their sample to either of those temperatures, they thought that they would see something akin to one of them and that their experiment would probe the transition's microscopic mechanism.

To check the x-ray results, colleagues Benjamin Freyer and Mirabelle Prémont-Schwarz used ultrafast IR spectroscopy to probe the system's vibrational modes. They found that the

bending mode of the NH_4^+ ion decreased in intensity, and then increased again, over the same time scale as the electron-proton transfer shown in the diffraction studies. They also confirmed that the system returned to its equilibrium structure within 500 ps—well before the next pump pulse was due to arrive 1 ms later.

That the team was able to see the motion of single electrons and protons is extremely promising; light atoms such as hydrogen are often invisible in diffraction studies. Still, the x-ray researchers are working with mechanical

engineering colleagues on campus to further improve the experiment's x-ray flux. They plan to turn their attention to the transition-metal complexes relevant to photovoltaic cells.

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Radio waves map matter without counting galaxies

A new technique for charting the large-scale structure of the universe has received its first experimental demonstration.

As everyone except movie directors knows, sound doesn't travel in outer space. But there was a time, spanning the first 380 000 years after the Big Bang, when acoustic waves did traverse the cosmos, which was filled with hot, dense plasma. As the plasma cooled and neutral atoms formed, the waves suddenly stopped propagating. Their mass-density pattern froze in place, and

the denser regions eventually contracted under their own weight to form galaxy clusters.

Cosmologists are interested in studying that density pattern—the so-called baryonic acoustic oscillations (BAOs)—as a way of tracing the universe's expansion. (See the article by Daniel Eisenstein and Charles Bennett, *PHYSICS TODAY*, April 2008, page 44.)

Observations of distant supernovae have led to the surprising conclusion that the expansion is accelerating under the influence of an enigmatic dark energy. (See the article by Saul Perlmutter, *PHYSICS TODAY*, April 2003, page 53.) But the expansion trajectory is poorly constrained. BAO observations could add further confirmation to the acceleration and perhaps provide some clues

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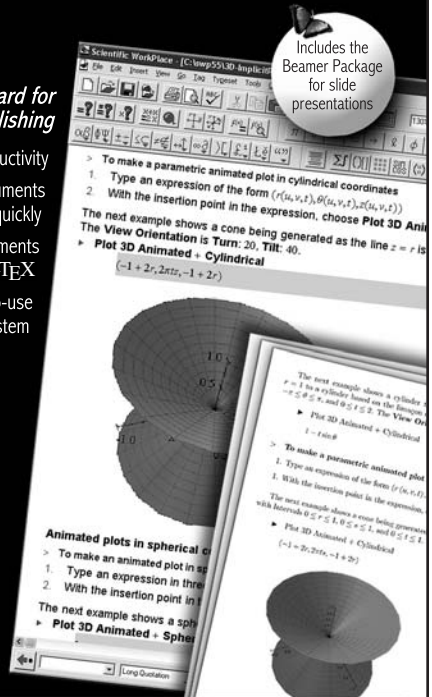
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