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Science 2 February 2007:
Vol. 315, no. 5812, pp. 609 - 610
DOI: 10.1126/science.1136895

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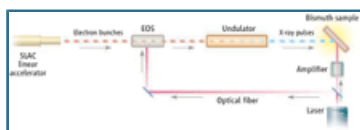
Watching Atoms Move

Joel D. Brock*

For more than a century, x-ray diffraction has provided detailed information on the structure of matter on atomic length scales. The recent advent of high-energy x-ray free-electron lasers (XFELs) now provides researchers the ability to watch matter move on both atomic length and time scales. On page 633 of this issue, Fritz *et al.* (1) report the use of ultrashort x-ray pulses from an XFEL to measure the dynamics of atomic vibrations in bismuth when excited by photons. These measurements provide researchers direct tests of calculations of highly excited electronic states and provide basic insights into our fundamental understanding of condensed matter.

Our understanding of the static or time-averaged structure of matter on atomic length scales has been dramatically advanced by direct structural measurements with x-rays. The current technical capability of x-ray crystallography is immense. The cover of *Science* regularly displays the structure of biologically important macromolecules determined through x-ray crystallography, and it is not unusual for these structures (e.g., viruses) to contain millions of atoms. However, the structure of matter is not static. Developing our understanding of the fundamental behavior of matter requires structural measurements on the time scales on which matter moves.

There are several important physical time scales of interest. Conformational relaxations in molecular systems and electron-lattice energy transfer in crystalline solids typically occur in a few picoseconds. Faster still are atomic vibrational periods, which are typically on the order of 100 femtoseconds. The characteristic time scale for electron-electron collisions in solids is on the order of 10 femtoseconds. And, quickest of all, are correlations in the dynamics of interacting electrons, which typically decay in less than 1 femtosecond. The key feature of all these time scales is that they are all "ultrafast"; that is, a few picoseconds or shorter.



Timing is everything. Experimental configuration for ultrafast x-ray diffraction. Bunches of electrons from a linear accelerator enter an XFEL undulator that generates short x-ray pulses. These are used to create diffraction patterns of the bismuth foil, which is heated by pulses from a laser. Electro-optical sampling (EOS) is used to detect the relative position in time of the x-ray and laser pulses, so that changes in bismuth lattice vibrations can be

determined precisely.

To date, ultrafast science has been the domain of femtosecond lasers operating at ultraviolet to infrared (IR) wavelengths. These wavelengths are not short enough for structural studies on atomic distances, and they are able to probe only those electronic states that extend over multiple atoms. However, building a suitable "hard" x-ray source (i.e., one that emits photons with wavelength in the range 1 to 2 angstroms, or an energy of about 10 keV) represents a major challenge.

For the past 35 years, the intense and highly collimated hard x-ray beams produced by synchrotron sources have been enormously successful both for static structural studies and for time-resolved studies down to the subnanosecond range. However, it is very difficult to create a useful ultrafast x-ray pulse with a conventional synchrotron because the equilibrium nature of an electron storage ring limits the electron-bunch length to the 10-picosecond range. Using state-of-the-art accelerator technology to "slice" the electron beam, researchers can generate ultrafast x-ray pulses (e.g., 200 femtoseconds) (2-4). The result is an ultrafast pulse of hard x-rays, but the slicing technique uses only a small fraction of the electrons in the bunch, dramatically reducing the flux. Consequently, there is a large worldwide effort to build linear accelerator (LINAC)-based ultrafast x-ray sources such as an XFEL or an energy recovery LINAC (ERL). XFEL and ERL sources circumvent the equilibrium electron-bunch size by using a LINAC rather than a storage ring.

Fritz *et al.* report femtosecond x-ray diffraction measurements performed at the Sub-Picosecond Photon Source (SPPS) at the Stanford Linear Accelerator Center (SLAC). The SPPS was a prototype XFEL built using the 2-mile-long LINAC at SLAC. These data represent the first real experimental glimpse into the behavior of materials at both atomic length and time scales. In their experiment, an ultrafast near-IR laser pulse photoexcites charge carriers in a bismuth crystal, which in turn excite one of the vibrational modes of the lattice--in this case, a coherent optical phonon (see the first figure). In essence, the nonequilibrium charge distribution abruptly alters the interatomic potential energy surface, thereby creating the force that drives the atomic motion. The dynamics of the resulting vibrational mode are determined by the shape of the nonequilibrium potential energy surface. Thus, by measuring the dynamics of the lattice motion, Fritz *et al.* are able to determine the (quasi)-equilibrium position and curvature of

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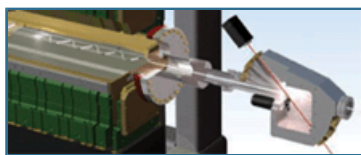
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the interatomic potential.



X-ray stopwatch. The relative temporal position of the electron bunches (white) interacts with an electro-optic crystal which, in turn, imprints a polarization transient on the laser (red) pulse.

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From a chemical point of view, having a fundamental understanding means understanding the adiabatic energy surface on which the constituent atoms move about during a chemical reaction. This is a very similar situation. We are watching the atoms move about after abruptly changing the potential energy surface. Thus, this experiment provides a clean, quantitative test of our current fundamental understanding of the interatomic potential energy surface of a highly excited atom as predicted by density functional theory.

On their way to making these measurements, the experimenters achieved several very important technical advances. The first was building and operating the SPPS. The second addressed a long-standing issue for pump-probe experiments with XFELs. One of the features of current XFEL designs is the generation of intense x-ray pulses by the self-amplified spontaneous emission (SASE) process. In SASE, density fluctuations in the electron bunch are amplified to make the pulse. Therefore, the pulses of x-rays vary in size, and there is no exact relation between the location of the electron bunch and the phase of the LINAC's radio frequency accelerating field. In this work, the researchers measured the arrival time of the x-ray pulse on a shot-by-shot basis with an electro-optic technique (5) (see the second figure). They then were able to use the pulse timing variation to obtain the relative delay between the pump laser pulse and the probe x-ray pulse, a vital piece of information in the experiments. Thus, they were able to turn what many predicted would be a major obstacle or challenge into a positive feature.

This clever use of XFEL beams will be critical to garnering the immense promise of these new sources. Chemists would like to make "movies" of reactions as molecules approach each other, form the intermediate transition states, and then relax into final products. Materials scientists would like to study the dynamics of events during thinfilm deposition. Condensed matter physicists would like to study the lowest-energy excitations of unusual systems such as high-temperature superconductors, heavy fermion systems charge- and spin-density wave systems (fractional), quantum Hall systems, and colossal magnetoresistance systems. And, of course, the grandest challenge of all is to understand in detail the electronic, structural, and chemical processes involved in photosynthesis.

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10.1126/science.1136895

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Science **315** (5812), 633. [DOI: 10.1126/science.1135009]

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