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Imaging Atomic Structure and Dynamics with Ultrafast X-ray Scattering

K. J. Gaffney1 and H. N. Chapman2

Measuring atomic-resolution images of materials with x-ray photons during chemical reactions or physical transformations resides at the technological forefront of x-ray science. New x-ray–based experimental capabilities have been closely linked with advances in x-ray sources, a trend that will continue with the impending arrival of x-ray–free electron lasers driven by electron accelerators. We discuss recent advances in ultrafast x-ray science and coherent imaging made possible by linear-accelerator–based light sources. These studies highlight the promise of ultrafast x-ray lasers, as well as the technical challenges and potential range of applications that will accompany these transformative x-ray light sources.

Many seminal advances in the natural sciences can be linked to the measurement of critical structures with atomic resolution. X-ray diffraction has proven to be among the most powerful tools for determining the atomic structures that catalyze fundamental advances in scientific disciplines ranging from biology to solid state physics. Although all objects scatter x-rays, crystal formation has been an essential step in the measurement of atomic-resolution structures for the majority of materials. Because of the regular arrangement of atoms in a crystal as opposed to an amorphous material, the x-ray scattering from the repeating structural unit adds coherently at periodically arranged Bragg peaks. This amplification greatly reduces the x-ray intensity required to measure a high-resolution diffraction pattern, but away from the Bragg peaks the scattered intensity remains too weak to measure, losing much of the information contained in the continuous molecular transform of the underlying structural unit. Even so, crystallography has remained the only method to measure diffraction at the large scattering angles required for the determination of high-resolution structures. The inability to crystallize important samples, however, has impeded progress in materials science and structural biology (1).

Measuring the continuous x-ray scattering pattern directly from a nonperiodic object, a lensless imaging technique inspired by crystallography, provides an alternative method for structure determination (2). This imaging technique requires the illuminating x-ray beam to maintain phase coherence across the entire width of the object, or across many repeating structural units in crystallography, in order to retrieve structural information. To coherently illuminate an object with the full fluence of an x-ray beam requires the source to possess laser-like properties.

For coherent imaging, as with crystallography, x-ray exposure determines the achievable resolution, and radiation damage sets the maximum dose. The necessity of limiting the dose without the benefit of Bragg amplification inhibits coherent imaging from achieving atomic-resolution imaging at synchrotrons designed to produce high average, but low peak, flux and has limited the technique to relatively large objects (3, 4), such as cells (5). Delivering the radiation dose to the sample in an extremely intense single x-ray pulse before the onset of radiation degradation provides a strategy for high-resolution x-ray imaging without crystallization (6, 7). Spontaneous synchrotron radiation cannot generate the peak coherent intensities necessary for imaging with a single pulse of light, but free electron lasers operating in the extreme ultraviolet have demonstrated that “instantaneous imaging” can be achieved (8) and x-ray–free electron lasers (XFEL) (9) have the promise of making atomic-resolution imaging possible (7).

More than sample preparation and radiation damage limit the utility of x-ray crystallography. An additional limitation has been the inability to observe atomic-level structure on the time scale of atomic motion. Direct visualization of these dynamics with x-ray scattering would greatly enhance our ability to study the nonequilibrium properties of materials and the pathways followed during infrequent equilibrium events, such as chemical reactions. Although time-resolved measurements have been made with use of the nominally 100-ps synchrotron pulses (10, 11), these sources are insufficient for single-shot diffractive imaging and for most measurements of structural dynamics. Single-shot x-ray imaging requires an extremely high per-pulse coherent flux, which can only be achieved with an x-ray laser, and both methodologies require fs duration x-ray pulses to image materials before the onset of x-ray damage and to temporally resolve atomic and molecular motions. Synchrotron pulses would need to be roughly a thousand times shorter than their typical duration to achieve this temporal resolution, which cannot be accomplished at standard beam currents.

Linear electron accelerators provide an alternative approach to generating x-rays that bypass the dominant limitations of synchrotrons. In a linear accelerator, the electrons do not recirculate, making it possible to generate a much brighter electron beam. Brightness represents the product of transverse spot size, divergence, energy spread, and pulse duration of a particle beam. The short electron pulse durations make it possible to generate fs x-ray pulses with per-pulse x-ray fluences comparable to those of synchrotrons. The Stanford Linear Accelerator Center (SLAC) built just such a facility, the Sub-Picosecond Pulse Source (SPPS), demonstrating the unique opportunity linear accelerators provide as ultrafast x-ray sources.

Whereas the SPPS generated spontaneous x-rays like a synchrotron, the tremendous brightness of linear accelerator electron beams makes lasing at x-ray wavelengths possible (12). The FLASH facility (13) at the Deutsches Elektronen Synchrotron currently generates extreme ultraviolet (UV) laser light with photon energies ranging from 20 to 200 eV. The Linac Coherent Light Source (LCLS) (14) at SLAC will be the world’s first XFEL starting in 2009, with other XFEL facilities scheduled to follow (15, 16). These facilities will generate x-ray photons with energies ranging from 800 eV to 12 keV.

The wavelength of the radiation at FLASH limits the spatial resolution to tens of nanometers. With the arrival of the LCLS and future facilities, x-ray beams with peak brightness 109 times brighter than that of current synchrotrons will be produced (17). This combination of high peak brightness, Å wavelengths, and fs pulse durations provide the necessary ingredients for pursuing atomic-resolution imaging and ultrafast science.

Femtosecond X-ray Scattering Studies of Structural Dynamics

Ultrafast laser spectroscopy has transformed our understanding of dynamics in the natural sciences. A few canonical measurements, coupled with theory and simulation, have provided robust atomic-scale descriptions of important structural transformations. However, for many important processes our interpretations remain largely speculative. This has driven the development of short-pulse x-ray (18–20) and electron (21) sources for probing dynamics.

For the majority of experimental studies of dynamics, a laser pulse initiates the transient phenomena by promoting electrons into non-equilibrium excited states. For ultrashort laser pulses, this electronic excitation impulsively modifies the potential energy surface of the atomic...
nuclei. This excited-state potential-energy surface determines the structural pathway followed after laser excitation. Determining the shape of the potential energy surface represents the critical, but generally difficult, objective of experimental studies of nonequilibrium structural dynamics.

The laser disordering and melting of semiconductors represent a classic demonstration of the limitations of optical studies and the potential of ultrafast x-ray sources for studying structural dynamics. Early experimental work demonstrated that intense fs pulse excitation of a silicon crystal led to a sub-ps increase in the reflectivity (22). Although absorption of the laser generates an increased reflectivity because of the direct excitation of carriers, the magnitude of the observed change could not be explained by this effect alone and led to the conclusion that intense laser excitation causes a semiconductor to metal transition. Because Si forms a metallic liquid, metal formation was attributed to crystal melting.

The rate of this purported phase transition exceeds the rate of energy transfer from the excited electrons to the crystal vibrations, leading to the supposition that the melting occurs nonthermally. Theoretical studies have supported this supposition by predicting that excitation of roughly half an electron per atom generates a crystal instability that spontaneously leads to crystal melting (23). Although ultrafast changes in the visible reflectivity led to this hypothetical nonthermal melting mechanism, these optical studies cannot unambiguously confirm the conjecture.

This puzzling situation made nonthermal melting a natural phenomenon for illustrating the viability of fs x-ray scattering (24). Studies of laser-excited InSb crystals with laser plasma-generated fs x-ray pulses observed a large amplitude decay of the (111) Bragg peak intensity in less than a ps (24). These measurements provided the first direct experimental evidence that large-scale atomic disordering proceeded concurrently with the large increase in optical reflectivity, but they could not identify the melting mechanism because of the limited source intensity.

The higher x-ray fluence and shorter pulse duration of the SPPS x-ray source provided a new opportunity to determine the mechanism for nonthermal melting of InSb (25–27). Initial measurements demonstrated that, for the first half ps after laser excitation, the atoms disorder inertially. The constant velocity dynamics of the ionic cores observed in the experiment occur with a thermal velocity distribution unchanged by laser excitation and generate large-scale increases in crystal disorder. Only at substantially higher carrier densities was accelerated disordering observed as predicted by theory (23, 27). Inertial dynamics do not, however, eliminate the ionic memory of the crystallographic lattice. The average atomic positions in the crystal have not changed, only the width of the distribution for the nuclei (Fig. 1, A and B). This demonstrates that the formation of a liquid requires collisions that randomize ionic momenta. The observation of diffusive atomic motion on the ps time scale suggests the emergence of liquid dynamics (26), but observing the formation and structure of the nascent liquid phase cannot be achieved with crystallography. Observing the short-range order of the liquid phase requires the measurement of diffuse scattering, as has been achieved with ultrafast electron diffraction measurements of laser melting of aluminum (28) and which could be carried out with an XFEL source.

Although linear accelerator–based ultrafast x-ray sources have higher per-pulse flux than alternative ultrafast x-ray sources (18–20), they lack the inherent time synchronization between the x-ray probe and the laser excitation pulse of these alternative sources. In a laser pump linear accelerator–derived x-ray probe measurement, the laser pulses must be synchronized to the x-ray pulses. Synchronizing the laser to the radio frequency field that accelerates the electrons nominally achieves this goal but does not ensure high-quality synchronization. The residual timing jitter between the x-ray and laser pulses results in shot-to-shot variations in their relative times of arrival that, when averaged over multiple pulse pairs, has a standard deviation of roughly 1 ps for the SLAC linear accelerator (29). Any experiment that averaged the signal from multiple pulses without accounting for this jitter would have ps time resolution, even with 100-fs pulses.

Seeing time synchronization as the primary technical challenge to studying ultrafast dynamics with x-ray laser sources, the SPPS collaboration developed an electro-optic sampling (EOS) technique for measuring timing jitter on a shot-to-shot basis by cross-correlating the laser pulses used for sample excitation with the electric field from the electron bunch used to produce the x-ray pulses (29). Ideally, the cross correlation would be between laser and x-ray pulses, but the weak x-ray–matter interaction makes this much more challenging. A laser pump x-ray probe investigation of coherent vibrational motion in a

**Fig. 1.** (A) Schematic representation of photogenerated softening of the interatomic potential in InSb (25). (B) Time-dependent distribution of atomic positions following bond softening. The initial Gaussian distribution broadens linearly with time and with a velocity determined by the root mean square atomic velocities before laser excitation. (C) Schematic representation of a photogenerated shift in the equilibrium bond length in a bismuth crystal (30, 34). (D) Time-dependent distribution of atomic positions after displacive vibrational excitation. The frequency of the coherently excited vibration determines the period of the oscillation in average atomic position, whereas the magnitude of the shift in equilibrium position determines the amplitude of the oscillation.
bismuth crystal confirmed the ability of the EOS measurement to accurately determine the shot-to-shot time delay (30).

In this study, fs laser pulse excitation of bismuth changes the equilibrium structure of the unit cell and leads to coherent vibrational motion (31–33) (Fig. 1, C and D). This coherent motion generates large-amplitude oscillations, in particular Bragg peaks such as the (111) reflection (34). This experimental observation of strong ~300-fs period oscillations in the (111) Bragg diffraction intensity rigorously demonstrated the utility of EOS as a timing diagnostic (29, 30). These measurements also provided a detailed characterization of the excited state potential, further demonstrating the utility of ultrafast x-ray scattering for the study of structural dynamics. Coherent vibrational motion in a ferroelectric crystal has also been observed with ultrafast x-ray diffraction by using laser-sliced x-ray pulses from a synchrotron (35). X-ray slicing sources represent an important development in ultrafast x-ray science with performance attributes distinct from XFEL sources. A complementary discussion of nonthermal melting and displacive excitations, as well as a discussion of data analysis, can be found in the Supporting Online Material (SOM) text.

**Coherent X-ray Imaging with Atomic Resolution**

Electromagnetic radiation can be used to image objects with a spatial resolution ultimately limited by the wavelength, \( \lambda \), of the radiation. Image formation can be simply described as interference; the light scattered by an object must be recombined so that it interferes at the image plane. Performing this reinterference directly with an aberration-free lens makes diffraction-limited imaging possible with visible radiation. In the simple case of illumination with a coherent plane wave, the achievable resolution equals \( d = \lambda / \sin \theta \), where \( \theta \) represents the highest scattering angle collected by a lens or detector. At x-ray wavelengths, however, manufacturing lenses that accept and redirect light scattered at high angles becomes increasingly difficult. Focal sizes of tens of nanometers can be achieved (36), but atomic-resolution lenses do not appear feasible.

Imaging at near-atomic resolution can be achieved without lenses by conducting the reinterference of the scattered light computationally. The numerical determination of the image from the measured x-ray scattering pattern requires that the phase of the diffracted light be determined in order to apply the correct phase shift to each reinterfering spatial frequency. Because the detection of the scattering pattern only measures the intensity of the scattering radiation rather than the amplitude, no phase information can be directly measured. A variety of methods have been developed for alleviating the information deficit in crystallography, such as examining the wavelength dependence of the diffraction pattern near an atomic absorption edge or by knowing part of the structure or a similar structure. With coherent diffractive imaging, an alternative route to reconstructing the scattered x-rays into an image can be used.

Sayre has noted that the continuous diffraction pattern of a coherently illuminated unit cell contains twice the information obtained from the diffraction pattern of a crystalline arrangement of identical copies of that unit cell (2, 37). If adequately sampled, this pattern provides the exact amount of information needed to solve the phase problem and deterministically invert the x-ray scattering pattern into an image of the scattering object. The past several decades have seen substantial advances in the experimental and numerical techniques re-

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**Fig. 2.** Schematic depiction of single-particle coherent diffractive imaging with an XFEL pulse. (A) The intensity pattern formed from the intense x-ray pulse (incident from left) scattering off the object is recorded on a pixelated detector. The pulse also photo-ionizes the sample. This leads to plasma formation and Coulomb explosion of the highly ionized particle, so only one diffraction pattern [a single two-dimensional (2D) view] can be recorded from the particle. Many individual diffraction patterns are recorded from single particles in a jet (traveling from top to bottom). The particles travel fast enough to clear the beam by the time the next pulse (and particle) arrives. The data must be read out from the detector just as quickly. (B) The full 3D diffraction data set is assembled from noisy diffraction patterns of identical particles in random and unknown orientations. Patterns are classified to group patterns of like orientation, averaged within the groups to increase signal to noise, oriented with respect to one another, and combined into a 3D reciprocal space. The image is then obtained by phase retrieval.
Radiation damage limits the highest resolution achievable with coherent diffractive imaging. When using 8-keV x-ray photons to image low atomic number materials such as a biomolecule, for every scattered photon that contributes to the diffraction pattern there are about 10 x-ray photons absorbed. This absorption deposits energy into the sample and leads to sample degradation. When exposed to high average brightness synchrotrons, biological materials can withstand doses of roughly 200 photons/Å², with cryogenic cooling. For a noncrystalline protein surrounded by vitreous ice, the number of scattered photons varies as 1/θ⁴. An exposure of 200 photons/Å² gives statistically significant signal only for feature sizes larger than d = 10 nm, much too coarse for imaging molecular or atomic structures, which have ångstrom scale features.

Delivering the radiation dose to the sample before radiation-induced structural degradation provides a strategy to exceed the exposure limit set by the radiation damage threshold at synchrotron facilities. Solem and Baldwin (6) first proposed x-ray laser flash imaging microscopy. Neutez et al. extended this concept to the use of XFEL pulses to image single nanoscopic particles at near-atomic resolution (7). They used a molecular dynamics simulation to model the interaction of a focused XFEL pulse on a single biomolecule. They simulated the influence of x-ray photo-ionization, electronic relaxation, illuminated particle charging, and the resultant Coulomb explosion while simultaneously calculating the x-ray scattering pattern (Fig. 2). They predict that x-ray lasers will allow fluences 10⁵ times larger for biological imaging than presently achievable with synchrotron radiation if the x-rays are delivered to the sample before the Coulomb explosion. This simulation indicates that the pulse will need to be tens of fs in duration or shorter for the explosion to have a minimal influence on the x-ray scattering pattern. For biological objects, the increased x-ray dose should allow single-pulse images to be acquired with about 1-nm resolution. Higher-resolution images will be achievable with more strongly scattering high-atomic-number materials. In addition to these molecular dynamics simulations, hydrodynamic calculations have modeled the influence of an intense ultrafast x-ray pulse on the atomic structure of a macromolecule or cluster (38, 39).

Despite the enormous increase in allowed fluence, atomic-resolution imaging of single particles will require averaging of multiple images (7, 40). This will need to be done serially, with a new, identical particle being delivered on every x-ray shot. Ideally, the particle should be the only scattering object in the beam path, requiring them to be introduced into vacuum and efficiently transported to the interaction volume. For randomly oriented particles, the requirement of orienting each single-pulse single-particle diffraction pattern sets the minimum scattering intensity. By following strategies similar to those used in single-particle cryoelectron microscopy (41), it will be possible to classify data into groups of similar orientation and vastly increase the signal-to-noise ratio by averaging. These classes must then be assembled into a three-dimensional coherent diffraction pattern (40), which will be phased (Fig. 2). Alternatively, the gas-phase particles could be aligned by a nonresonant laser pulse (42), greatly easing the single-pulse signal to noise required for computational alignment and averaging.

The single-pulse diffractive image of a micrometer-sized test object recorded at FLASH provides a dramatic illustration of the “flash” imaging technique (8) (Fig. 3). This demonstrates that an interpretable coherent diffraction pattern with excellent signal to noise can be collected from a small isolated object in a single FEL pulse. The focused pulse can destroy all material in its path, including the detector, and it was not previously obvious whether a diffraction pattern could be recorded without a large background resulting from scattering from a beam stop, from the focusing optics, or from plasma radiation from the sample. These effects were prevented by using a novel graded multilayer mirror that only reflects the elastically scattered light from the sample onto a charge-coupled device (CCD) detector located in the optical far field and harmlessly passes the strong undiffracted beam through a hole in the mirror. The pulse that recorded the diffraction pattern heated the sample up to about 60,000 K, which ablated and melted. Nevertheless, the image is recorded to the 62-nm diffraction limit of the detector aperture, showing no effects of damage. Compared with diffractive imaging at synchrotrons, which is difficult because of the low coherent flux available and the need to filter a single coherent mode from an incoherent source, imaging with the FEL is straightforward and requires no spatial or spectral filtering of the illuminating pulse.

**Future Prospects**

The importance of ultrafast x-ray scattering and imaging measurements extends beyond the particular phenomena and materials studied to date. Excited state potential energy surfaces govern the evolution of nonequilibrium systems and also the...
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dynamics and kinetics of rare events in equilibrium systems, such as thermal phase transitions and chemical reactions. The SPPS collaboration has demonstrated that fs x-ray scattering can determine the topography of the excited state potential energy surface with unprecedented detail. Despite the success of the SPPS collaboration, the low flux of the source determined the scope of the scientific program. At the LCLS, the integrated x-ray production in 10 s of lasing will exceed the total x-ray photon production at the SPPS during its 3-year lifetime.

The increased flux will make possible diffuse scattering measurements for a wide variety of materials. For the vast majority of ultrafast phenomena, the transformations in structure will be localized in space and occur on the angstrom length scale. These changes in short range order will be manifest in the diffuse scattering. Femtosecond-resolution diffuse scattering measurements will be particularly important for studies of solution phase chemical dynamics (11) and order-disorder phase transition studies (28). Learning how to exploit the coherence of the x-ray pulses for studies of dynamics will also be an important aspect of the initial science programs at XFEL facilities. With coherent imaging techniques, the absolute structure, not just the average structure, can be measured. This should prove to be an important attribute for the investigation of first-order phase transitions, where deviations from the average structure, such as defects and imperfections, nucleate phase transformations. Time-resolved FEL imaging with an ultrafast optical pump will follow from practices developed at synchrotron slicing sources and the SPPS. Techniques for pumping samples with FEL pulses and probing the resultant dynamics with time-delayed FEL pulses will require further experimental development. One promising approach involves splitting the FEL pulse at or near the sample with use of a section of an optical element destroyed by the FEL pulse, along with the sample (45). Despite the many experimental and technical challenges that will exist at x-ray-free electron laser sources, the unprecedented peak brightness of XFEL radiation should open the field of ultrafast x-ray science to a range of applications and phenomena approaching those studied with ultrafast lasers and x-ray synchrotrons.

The field of coherent x-ray diffractive imaging will benefit tremendously from the construction of x-ray laser sources. The FLASH free electron laser has demonstrated the feasibility of "instantaneous" imaging and provided a unique opportunity to prepare for the enormous peak brightness and power needed for atomic-resolution imaging. Major technical and experimental advances have been achieved in the past 2 years, although many challenges remain. These advances, in conjunction with the expected flux and time resolution of x-ray laser sources, will enable x-ray imaging with unprecedented spatial resolution. With XFEL sources, the dream of atomic-resolution imaging may become reality.

References and Notes
9. An x-ray–free electron laser uses a fs-duration bunch of high-energy electrons as the gain medium in a single pass laser. Acceleration of these high-energy electrons in an oscillatory magnetic field causes the electrons to spontaneously emit x-ray photons. This radiation emitted in the first few periods of the magnetic field interacts with the electron bunch, causing it to form many microbunches. Each microbunch within the fs-duration macropulse emits coherently, creating many sub-fs pulses of x-ray light contained within a roughly 100-fs-duration macropulse.
16. www.xfel.spring8.or.jp/.
17. Brightness provides a particularly important metric for single-shot imaging, because brightness determines the instantaneous x-ray flux on an extremely small sample.
44. K. J. G. thanks the SPPS collaboration, in particular J. B. Hastings, A. M. Lindenberg, and D. A. Reis, as well as the U.S. Department of Energy (DOE) and the W. M. Keck Foundation for financial support. H.N.C. thanks J. Hajdu and Lab-Directed Research and Development support at Lawrence Livermore National Laboratory. This work was performed in part under the auspices of the DOE by the University of California, Lawrence Livermore National Laboratory, under contract W-7405-Eng-48.

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SOM Text
Fig. S1
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