

By combining traditional x-ray techniques for structural determination with the time resolution of ultrafast laser spectroscopy, researchers are beginning to measure atomic rearrangements directly.

Femtosecond X-Ray Diffraction

ANDREA CAVALLERI
CRAIG W. SIDERS
KLAUS SOKOLOWSKI-TINTEN
CSABA TÓTH
CHRISTIAN BLOME
JEFF A. SOQUIER
DIETRICH VON DER LINDE
CHRISTOPHER P.J. BARTY,
and KENT R. WILSON

With the discovery of x rays in 1896,¹ scientists gained the ability to resolve atomic arrangements² of increasingly complex systems. The importance of x rays can hardly be overemphasized: over the course of the last century, they have provided most of our knowledge of the static structure of matter, from simple systems³ to the complex macromolecules responsible for carrying out biological functions. Yet most fundamental processes in nature, including chemical and biochemical reactions or phase transitions, involve dynamic changes in the structural properties of matter and atomic rearrangement. These changes usually occur on ultrafast time scales, comparable to the natural oscillation periods of atoms and molecules. This time frame, ranging from a few tens of femtoseconds to picoseconds, has been accessible for more than two decades through the use of ultrashort pulses in the visible frequency range.^{4,5} But the structural properties of matter are only indirectly accessible through the use of optical pulses: in fact, inasmuch as light at visible frequencies is sensitive only to the dynamics of valence electrons, it carries little information with regard to the actual structural properties of matter.

Because keV-range x rays couple directly with the core electrons spatially localized around each nucleus, they are sensitive to atomic arrangement. Thus, the availability of ultrashort (fs and ps) x-ray pulses opens new possibilities for time-resolved studies of structural rearrangements. For this reason much effort is dedicated to the production, optimization, and application of femtosecond hard x-ray pulses.

By combining traditional techniques for structural determination with the time resolution made possible by ultrafast laser spectroscopy, researchers will be able to take direct measurements of atomic rearrangements to determine fundamental processes in physics, chemistry, and biology. Perhaps the most emblematic example, although by no means the only one, is the extension of x-ray diffraction measurements to the ultrafast time scale. Figure 1 provides an intuitive representation of the technique: while a visible or near-visible laser pulse initiates the dynamics in the ensemble under investigation, a synchronized, appropriately delayed x-ray pulse is diffracted at a particular instant to “photograph” the structure.

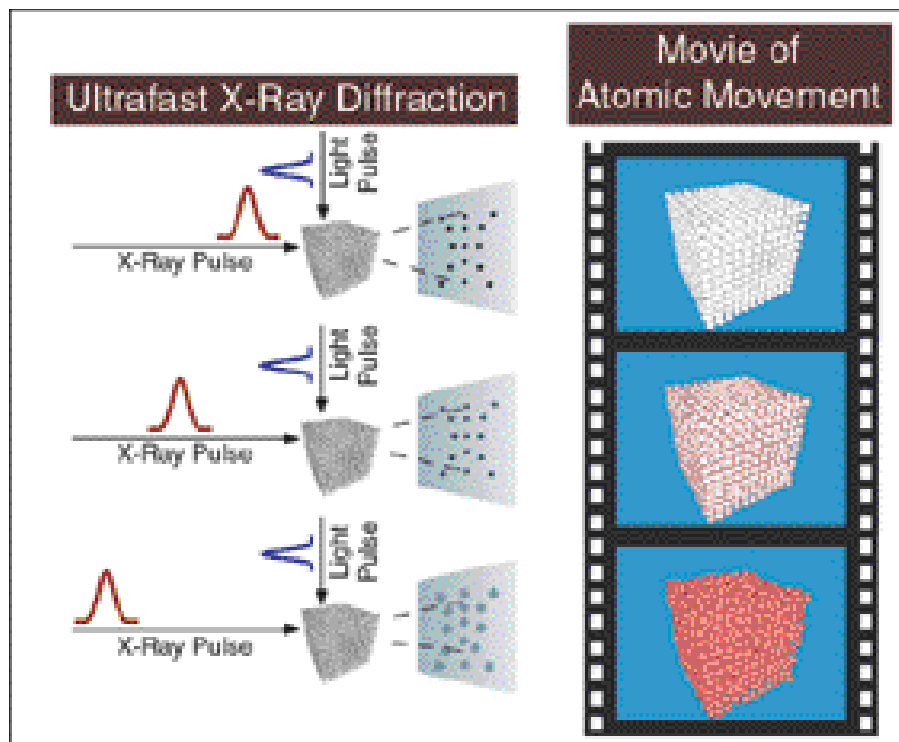


Figure 1. Intuitive representation of an ultrafast x-ray diffraction experiment. Ideally, after excitation with a short laser pulse, the transient structure of a dynamically evolving system is measured at each time delay.

Ultrashort x-ray pulses

Until recently, it was not possible to produce hard x-ray pulses of a duration shorter than several tens of picoseconds. For the past decade, researchers have dedicated extensive resources to the achievement of this goal. The techniques used to generate ultrafast x-rays in the subpicosecond regime can be divided into two categories:

1. Femtosecond-laser-driven-plasma sources: The development of chirped-pulse amplification⁶ has enabled efficient amplification of femtosecond laser pulses in solid-state materials such as TiAl_2O_3 and has also led to the development of tabletop terawatt-class lasers.⁷ When focused onto solid targets, femtosecond terawatt lasers generate high-density microplasmas that are capable of emitting subpicosecond pulses of hard x-ray radiation.^{8,9} The mechanism by which these pulses are produced does not substantially differ from that which occurs in a traditional x-ray tube, where a static electric field accelerates electrons, generating line radiation and continuous bremsstrahlung on collision with a solid target. In the case of laser-produced plasma sources, the free electrons generated by laser-induced ion-

ization are also accelerated to near-relativistic velocities by the same laser pulse. Characteristic radiation is therefore emitted for a time determined by the duration of the electron bunch (approximately equal to that of femtosecond laser pulses). By using a number of target materials, it has been shown that femtosecond-laser-driven-plasma sources produce monochromatic x-ray pulses in the kilo-electron-volt range. Such sources can be used to resolve structural dynamics that occur within a few hundred femtoseconds.¹⁰

2. Synchrotron sources: The combination of ultrafast laser technology and synchrotron radiation has allowed researchers to achieve a number of advances in the generation and application of ultrafast x-ray technology. We briefly reference some of the most important ones, pioneered largely by our colleagues at Lawrence Berkeley National Laboratory in a collaborative effort built around the Advanced Light Source:

- (a) it has been shown that 90° Thomson scattering between infrared terawatt laser pulses and relativistic electrons from an accelerator produce 300-fs, broadband 30-keV pulses^{11,12};

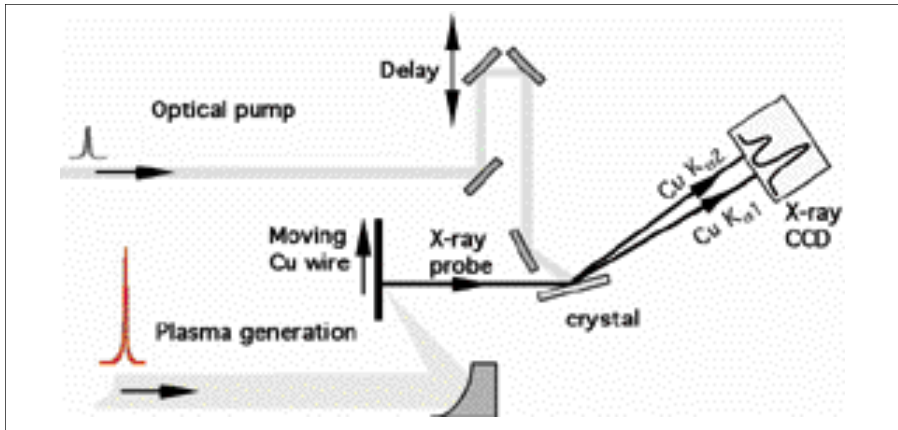


Figure 2. Setup for the visible pump, x-ray probe experiments. Terawatt laser pulses are focused onto a moving metallic wire to produce short x-ray bursts, which are then diffracted by an excited semiconductor at different time delays from the optical pump. The 30-fs, 800-nm laser pulses are generated at 20 Hz by an ultrafast Ti:sapphire laser. The output of the laser is used for both sample excitation and x-ray generation. The latter is done by focusing the pulses onto a moving Cu wire in vacuum, resulting in a point source of Cu K_{α} photons. The radiation emitted, which consists of two closely spaced $K_{\alpha 1}$ and $K_{\alpha 2}$ lines, is diffracted from the optically pumped Ge and detected by an x-ray CCD camera. An ultrashort pulse of laser-generated Cu K_{α} x-rays diffracts in a symmetric Bragg configuration from Ge, penetrating ~ 2 mm into the bulk along the surface normal. In addition to the bulk Ge crystal shown, Ge-Si heterostructures are used.

- (b) gating of a 70 ps x-ray pulse diffracted from an optically pumped semiconductor crystal has been achieved by taking advantage of ultrafast, laser induced disordering of semiconductors.¹³ (Other x-ray switching techniques, involving scattering from coherently controlled optical phonons in semiconductors, have been proposed)¹⁴;
- (c) a jitter-free x-ray streak camera has been demonstrated to improve the multishot time resolution of synchrotron pulses to approximately 2 ps (Ref. 15);
- (d) finally, the interaction of laser pulses with the electron beam within the storage ring of a synchrotron¹⁶ has recently been shown¹⁷ to be a practical source to produce 100-fs x-ray pulses continuously tunable across the spectrum of synchrotron radiation.

Studies of lattice dynamics in crystalline solids

In this article, we summarize some of the results achieved over the past few years through a collaboration between the University of California, San Diego and the University of Essen, Germany. In our two laboratories, terawatt laser pulses focused onto moving metallic wires provide convenient, multiple kilo-electron-volt ultra-

fast x-ray sources. X-ray bursts produced in this manner have been used in a series of optical pump and x-ray probe experiments in crystalline solids. Direct measurements of lattice dynamics were performed during vibrational energy transport and phase transformations.

Acoustic dynamics in bulk semiconductors

Acoustic phonons in solids are fundamentally important because, unlike optical phonons, they are responsible for the transport of vibrational energy (coherent sound waves or heat). They are also the last step in the thermalization pathway following optical excitation, with the energy flowing from the hot carriers to optical phonons and finally to acoustic excitations of the lattice. But although the ultrafast processes that involve charge carriers and Raman-active optical phonons can be probed by use of optical methods, acoustic phonons have remained largely undetected. Using short-pulse x-ray diffraction, our experiments could resolve ultrafast strain dynamics (i.e., spatially and tem-

porally dependent lattice deformations) within various solids, allowing measurements of the evolution and dephasing of coherent acoustic phonons. We measured the angle- and time-dependent x-ray reflectivity of the photo-pumped samples using an 8-keV, copper-based ultrafast x-ray source as a function of time delay (see Fig. 2). The experimental results obtained for bulk Ge (111) can be seen on the left-hand side of Fig. 3. In brief, during the first picosecond (or the first few picoseconds) following optical excitation, the photoexcited hot carriers interact with the lattice and increase its temperature. This occurs faster than acoustic expansion of the crystal can take place, resulting in heating at a constant volume. At this point, the pressure of the crystal increases (i.e., the solid is stressed) but almost no change in lattice spacing (i.e., strain) has taken place. Surface expansion occurs later at the speed of sound (5400 m/s or 5.4 nm/ps in Ge). Figure 4 provides an intuitive representation of the first stage after deposition of the optical energy: the color code represents expansive (red) and compressive (blue) strain; temperature and stress are not shown. After coherent acoustic expansion, a layer with a new lattice constant forms at the surface, which results in the appearance of a shoulder to the left of the diffraction lines, at the new Bragg angle for the surface layer [see Fig. 3(a)]. Later, a picosecond acoustic pulse forms and propagates into the bulk of the solid, leaving expansive thermal strain at the surface¹⁸ and causing the shoulder in the x-ray data to merge with the main diffraction lines. Figure 3(b) shows the result of a model calculation, performed along the lines discussed above. Starting from the expected initial

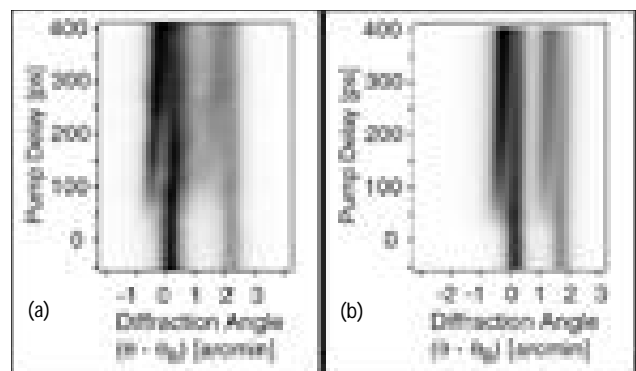


Figure 3. Measurement of coherent acoustic dynamics in bulk germanium. (a): measured rocking curve of dynamically strained germanium as a function of optical pump and x-ray probe time delay. (b): calculated time-dependent rocking curve.

temperature profile, we solved the elastic and heat equations, yielding the evolution of the strain profile and of the resulting diffraction. The close agreement between the model and the experimental data demonstrates that our technique allows for quantitative measurement of ultrafast, coherent lattice dynamics in solids, achieved with picosecond time and milliangstrom strain resolution.¹⁹

Acoustic dynamics in semiconductor heterostructures

Thus, ultrafast x-ray diffraction can be used to study lattice transport deep within the bulk of solids and on the natural timescale of atomic vibrations. This capability encouraged us to extend our studies to semiconductor heterostructures. These systems, composed of layers of different materials grown in sandwichlike structures, constitute the basic building block of modern electronic and optical devices. In our experiments, we used simple structures composed of germanium thin films of different thicknesses grown heteroepitaxially on bulk silicon substrates. By taking advantage of the 4% difference in lattice constant between germanium and silicon, we were able to measure (111) diffraction at two separate angles and to simultaneously detect acoustic dynamics in the two solids. Femtosecond pump pulses were used selectively to excite the surface Ge film, homogeneously heated by photogenerated hot carriers. Because these carriers were isolated from the substrate by the 430-meV potential energy barrier at the buried interface, the bulk silicon was initially left completely unexcited, whereas the Ge film was instantaneously heated at a constant volume. Figure 5 shows the resulting shifts of the diffraction lines, summarized by their centroid positions. In brief, the existence of two interfaces with discontinuous elastic properties (vacuum-Ge and Ge-Si) defines an acoustic cavity within the Ge layer and dictates the oscillatory evolution of the strain with period given by $2L/c$, where L is the film thickness and c is the speed of sound. A corresponding shift of the silicon line toward higher diffraction angles is caused by compressive recoil of the substrate, or, in other words, by coherent vibrational energy transport through the interface.

The peak magnitude of the compressive strain is of the order of 0.006%, which corresponds to an absolute change in interlayer spacing of approximately 20 fm, a

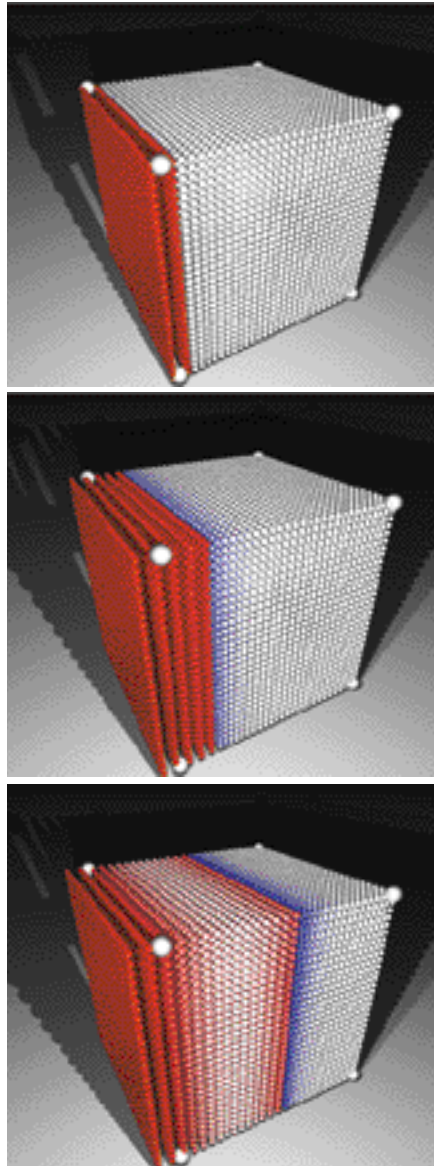


Figure 4. Intuitive representation of the strain profile in GaAs after impulsive heating. The laser pulse impinges on the crystal surface from the left-hand side of the figure. Each lattice plane indicated in the figure corresponds to many thousands of real lattice planes. The red regions of the crystal undergo expansive strain; the blue regions are compressed.

few nuclear diameters. Later, incoherent diffusive heat transport was observed, as evidenced by the slow recovery of the Ge centroid toward the Bragg angle of the cold solid and by a shift of the Si centroid toward lower diffraction angles, caused by progressive heating of the substrate. The fluence dependence of the oscillation decay rates was used to retrieve the tempera-

ture-dependent anharmonic dephasing of acoustic phonons within the germanium film. We attributed the observed damping to T_2 processes that originate in large part from four phonon interactions and cause the observed loss of coherence in the 7-GHz acoustic phonon mode.²⁰

Ultrafast melting in semiconductors

A second objective of the San Diego and Essen groups' collaboration was to measure the disordering time during ultrafast melting. In brief, ultrafast melting is known to follow two different physical pathways, depending on the initial density of excited carriers.²¹ In the case of near-threshold femtosecond-pulse energies and for pulses that are longer than a few picoseconds, melting is thermal, following a quasi-equilibrium physical pathway. Carriers thermalize with the lattice and bring the temperature of the crystal above the equilibrium melting temperature. In this case, the liquid phase is nucleated first at the surface, around defects and inclusions. Melting then proceeds into the bulk of the crystal and a liquid-solid interface propagates at a speed that is dictated by the degree of superheating of the interface ($T_{\text{solid}} > T_{\text{melting}}$) and strictly limited by the speed of sound. This requires use of several hundreds of picoseconds to melt a few tens of nanometers. For femtosecond pulses of higher fluence,²² melting proceeds as a nonthermal, ultrafast process, in which lattice destabilization is caused by excitation of a dense, electron-hole plasma.²³ In this case complete melting is expected to occur on a subpicosecond time scale over a layer of several tens of nanometers.

Since optical measurement techniques do not resolve atomic dynamics during phase transition, characterization of optical properties is still an indirect measurement of the disassembling crystal. Substantial effort toward the measurement of ultrafast melting has been made by a number of groups with regard to the time resolution of this process using ultrafast x-ray diffraction. Two major shortcomings have generally limited the results we achieved as well as the types of material that could be investigated. First, experiments were performed on bulk samples, in which the depth over which the visible pump light can induce melting is generally approximately 1 order of magnitude smaller than the penetration depth of the x rays. For this reason, the thickness of the optically

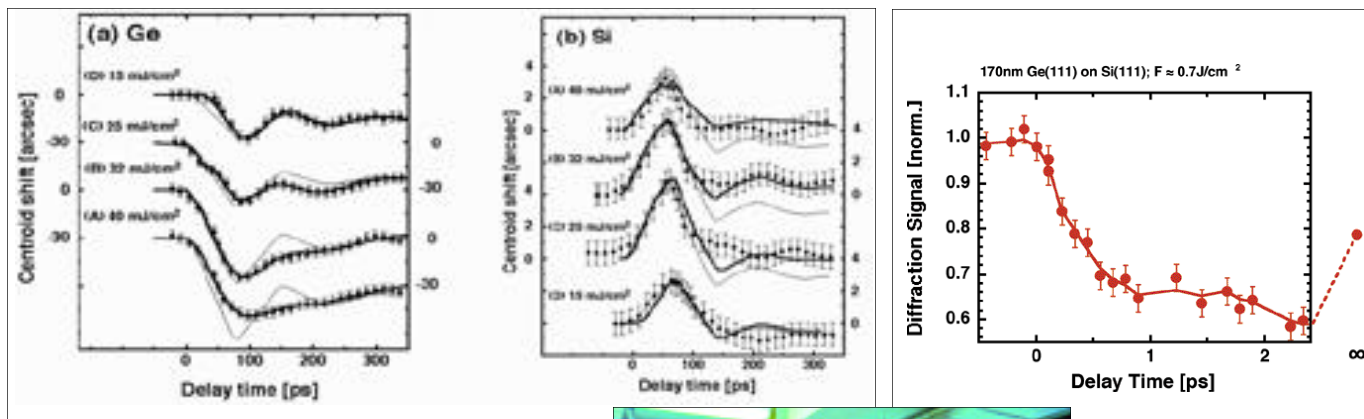


Figure 5. Measurement of coherent acoustic dynamics in Ge-Si heterostructures. Shift of the centroid of diffraction as a function of time, after optical excitation with femtosecond laser pulses of a 400-nm Ge film grown on a Si substrate. The response of the Ge film (left) indicates damped oscillatory expansive strain dynamics with a period of $T = 150$ ps. The Si substrate (right) recoils with synchronous compression. The thin curve is the calculated response of the heterostructure, assuming that the acoustic dynamic behaves harmonically, i.e., without dephasing. The thick curve in Fig. 5(a) is the result of a fit to the germanium data, which means that the heating time and anharmonic damping are free parameters. The thick curve in Fig. 5(b) is the calculated response of the silicon that was obtained with the best-fit parameters extracted from the dynamics in Ge.

Craig Siders and Andrea Cavalleri next to the chamber where the x rays are produced.



Figure 6. Measurement of non-thermal melting in germanium. Integrated diffraction yield as a function of visible pump-x-ray probe delay, normalized to the signal from the unpumped crystal. Continuous line: guide to the eye. We recorded this set of data at the University of Essen using a 4.5-keV-femtosecond x-ray source and toroidally bent diffraction crystals as the focusing element.

and compactness of ultrafast x-ray systems have

molten surface layer is in most cases a small fraction of the probed depth, causing a small reduction in the overall diffraction yield. This limits the number of bulk materials that can be investigated to a subset in which the x-ray penetration depth is limited by photoelectric absorption. Second, because of the high repetition rates, the samples could not always be translated after each laser shot, causing cumulative damage and poorly controlled experimental conditions. The availability of *large samples* of a single crystal 155-nm *thin-film* germanium grown on silicon and of a focusing optic based on a toroidally bent semiconductor has enabled us to overcome both experimental problems. First, by using thin Ge films, we were able to match the depth pumped and probed by the laser pulse and x rays, demonstrating measurements that can now be extended to a broad variety of solids. Second, the focusing optic allowed delivery of approximately 2×10^4 monochromatic Ti-K $_{\alpha}$ photons/pulse onto the pumped and probed spot, permitting nearly single-shot measurement of x-ray reflection from Ge.

We were able to translate the sample after each shot, acquiring data with the same

standards routinely used in ultrafast *optical* studies of nonreversible dynamics of solids. As shown in Fig. 6, the diffraction signal drops significantly within a few hundred femtoseconds in the region in which the pump intensity is high enough to cause *homogeneous* ultrafast melting on a thick layer. We have also demonstrated that the outer area melts over the same thickness on a significantly longer time scale, indicating thermal inhomogeneous melting.²⁴ A rapid response is visible at early times, indicating that a 50-nm layer has *homogeneously* lost crystalline order within a few hundred femtoseconds.²⁵ For longer periods of time, part of the crystalline order is reestablished, indicating resolidification into a (111) crystal and corroborating the interpretation of the subpicosecond data as a solid-to-liquid phase transition, as opposed to plasma formation at the surface.

Conclusions and future directions

The ability to amplify femtosecond laser pulses to terawatt levels has, in addition to many other applications, enabled the generation of ultrashort hard x-ray pulses in small-scale laboratories. The simplicity

stimulated their widespread application in the measurement of structural dynamics in materials. The study of lattice transport and phase transitions in simple crystalline solids has now been demonstrated in a number of laboratories across the world and can be said to constitute a mature experimental technique. Future challenges include dynamic diffraction experiments in less ordered or more complicated systems, such as powders, amorphous solids, and possibly liquids or protein crystals.²⁶ The availability of ultrafast continuum or tunable sources would open new frontiers, because it would allow extension of absorption measurements to the femtosecond time scale,²⁷ ultimately providing a tool to investigate dynamic changes in the immediate, disordered environment of single atoms or molecules. Some of these experiments will most likely be made possible by incremental changes in existing technologies. On the other hand, extension to complex chemical and biochemical dynamics²⁸ will require substantial improvements in experimental tools, particularly in terms of total flux and tunability across the x-ray spectrum.

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Andrea Cavalleri is with the Materials Science Division, Lawrence Berkeley National Laboratory. He can be reached by e-mail at acavalleri@lbl.gov. Craig Siders is with the School of Optics, CREOL at the University of Central Florida. Csaba Tóth is with the Center for Beam Physics, Lawrence Berkeley National Laboratory. Jeff Squier is with the University of California San Diego. Christopher P.J. Barty is with the Lawrence Livermore National Laboratory. Klaus Sokolowski-Tinten, Christian Blome and Dietrich von der Linde are with the Institut fuer Laser und Plasmaphysik, University of Essen, Germany.

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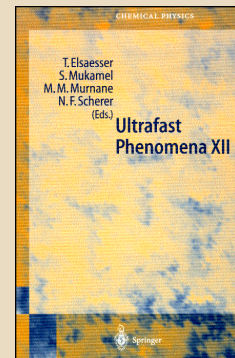
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