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Picoscience dynamics of laser-induced strain in graphite

M. Harb,1 A. Jurgilaitis,1 H. Enquist,2 R. Nüske,1 C. v. Korff Schmising,1 J. Gaudin,3 S. L. Johnson,4 C. J. Milne,5 P. Beaud,4 E. Vorobeva,4 A. Caviezel,4 S. O. Mariager,4 G. Ingold,4 and J. Larsson1,5

1Atomic Physics Division, Department of Physics, Lund University, P.O. Box 118, 22100 Lund, Sweden
2MAX-lab, Lund University, P.O. Box 118, Lund, Sweden
3European XFEL GmbH, Albert-Einstein-Ring 19, D-22761 Hamburg, Germany
4Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
5Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

We report on the use of grazing-incidence time-resolved x-ray diffraction to investigate the evolution of strain in natural graphite excited by femtosecond-laser pulses in the fluence range of 6–35 mJ/cm². Strains corresponding to up to ∼2.8% c-axis expansion were observed. We show that the experimental data is in good agreement with calculations based on the Thomas strain model in conjunction with dynamical diffraction theory. Furthermore we find no evidence of nonthermal lattice expansion as reported in recent ultrafast electron-diffraction studies of laser-excited graphite conducted under comparable excitation conditions.

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I. INTRODUCTION

Ever since the discovery of fullerenes there has been an explosive interest in the synthesis of carbon-based materials, placing these materials at the forefront of the nanoscience revolution. Today carbon-based materials are the basis for numerous novel technologies including graphene based nanoelectronics1 and nanofluidics in carbon nanotubes.2 At the most basic level the existence of different carbon allotropes in graphite gives rise to nonthermal strains, an alternative mechanism that includes the anisotropic population of carriers in the electronic band and the subsequent generation of coherent optical-phonons. The results reported by Carbone et al. started a debate within the scientific community on whether the observed shifts in the positions of the diffraction spots represent real structural dynamics or are somehow related to transient electric fields generated at the surface of the sample because of the ejection of electrons by the laser pulse. Park et al. investigated the effects of transient-electric fields on an electron-probe pulse both experimentally and through simulations and concluded that these fields can indeed deflect the electron probe in a way consistent with the dynamics observed in Carbone’s work. The claims of Park et al., however, were recently disputed. In yet another graphite study by Raman et al., performed under similar excitation conditions and using the same technique of UED, even larger amounts of shifts in the positions of the diffraction spots were reported, corresponding to 6% expansion of the interlayer distance at an excitation fluence of 40 mJ/cm². Raman et al. attributed the shifts partially to structural dynamics and partially to surface charging of the sample and presented a model of the surface potential, which was used to separate the two effects. It is evident from the foregoing survey of conflicting results that in order to settle the question of whether or not laser excitation of graphite gives rise to nonthermal strains, an alternative approach is needed. A new technique that can probe real structural dynamics on the relevant femtosecond to picosecond timescales and offer extraordinary insights into the complex and competing channels of relaxation that follow the interaction of laser with matter.

In a recent study by Carbone et al., laser-excited graphite was investigated using ultrafast electron diffraction (UED) in reflection geometry. Carbone and coworkers observed contraction of the graphite lattice along the c axis at the onset of excitation, followed by expansion of up to 1.25% of the interlayer distance at the highest fluence of 44.5 mJ/cm². It was argued that such a large amount of lattice expansion cannot be accounted for by linear-thermal expansion alone. Instead, the authors attributed the expansion to nonthermal mechanisms that include the anisotropic population of carriers in the electronic band and the subsequent generation of coherent optical-phonons. The results reported by Carbone et al. started a debate within the scientific community on whether the observed shifts in the positions of the diffraction spots represent real structural dynamics or are somehow related to transient electric fields generated at the surface of the sample because of the ejection of electrons by the laser pulse. Park et al. investigated the effects of transient-electric fields on an electron-probe pulse both experimentally and through simulations and concluded that these fields can indeed deflect the electron probe in a way consistent with the dynamics observed in Carbone’s work. The claims of Park et al., however, were recently disputed. In yet another graphite study by Raman et al., performed under similar excitation conditions and using the same technique of UED, even larger amounts of shifts in the positions of the diffraction spots were reported, corresponding to 6% expansion of the interlayer distance at an excitation fluence of 40 mJ/cm². Raman et al. attributed the shifts partially to structural dynamics and partially to surface charging of the sample and presented a model of the surface potential, which was used to separate the two effects. It is evident from the foregoing survey of conflicting results that in order to settle the question of whether or not laser excitation of graphite gives rise to nonthermal strains, an alternative approach is needed. A new technique that can probe real structural dynamics on the relevant femtosecond to picosecond timescales and offer extraordinary insights into the complex and competing channels of relaxation that follow the interaction of laser with matter.
approach to UED is warranted. To this end, here we investigate the structural dynamics of laser-irradiated graphite using time-resolved x-ray diffraction. X rays make an ideal structural probe in this context as they are insensitive to transient-electric fields that may be generated at the surface of the sample.

II. EXPERIMENTAL SETUP

The experiment was carried out at the Swiss Light Source (SLS). The FEMTO slicing-source at SLS generates 140-fs x-ray pulses through laser slicing of the electrons in the insertion device. The overall time resolution of the pump-probe scheme is dictated by the duration of the x-ray probe and laser-pump pulses, the timing jitter of the laser system, and the geometrical mismatch angle between pump and probe beams. An overall time resolution of <200 fs has been demonstrated in several recent studies performed at this beamline (e.g., see Johnson et al.23). The sample used in our study is a mined natural graphite flake, which was cleaved to produce a surface with high-quality flatness. The single-crystalline nature of the sample was verified through static x-ray diffraction measurements carried out at beamline D611 at MAX-lab. For the time-resolved measurements, the x-ray source was tuned to an energy of 5.85 KeV with ~1% bandwidth and focused to a spot size of ∼300 × 10 μm². To match the x-ray penetration depth with the optical-absorption depth in graphite, we employ the noncoplanar-diffraction geometry with extreme (near critical angle) grazing incidence shown in Fig. 1(a). The grazing angle (ϕi) was set by first calculating the corresponding vertical displacement of the specularly reflected x-ray beam relative to the direct beam on a screen positioned at known distance from the sample. An avalanche photodiode (APD) was then placed at the set displacement and the intensity of the specularly reflected x-ray beam was maximized by varying ϕi. Measurements were conducted at two different grazing angles below (0.27°) and above (0.50°) the critical angle of 0.30°. The sample was excited at fluences ranging from 6–35 mJ/cm² with p-polarized 120-fs-laser pulses centered around 800 nm and incident at 10° relative to the sample surface. The 0.75 × 4.5 mm² footprint of the laser beam on the sample was sufficiently large to cover the 0.3 × 2 mm² x-ray footprint, ensuring homogeneous excitation of the probed area. X-ray rocking curves were recorded at selected time delays in the −10 ps to +100 ps range by measuring the intensity of the 101 reflection with an APD as function of the sample in plane rotation (θi). The respective repetition rates of the x-ray probe and laser-pump pulses of 2 KHz and 1 KHz imply that every other x-ray pulse contributes to a reference (unpumped) signal. Figure 1(b) shows the 101 rocking curve of the unpumped sample at a grazing angle of 0.27°.

III. RESULTS AND THEORETICAL MODEL

Results of time-resolved measurements are shown in Fig. 2 in the form of rocking-curve differences at selected time points both below (a–f) and above (g–l) critical angle and for an incident excitation fluence of 26 mJ/cm². It is evident from the time-dependent shift of the rocking curves that the graphite lattice is strained. To explain the detailed shape of the curves, modeling of strain-wave propagation and x-ray scattering is needed. We employ the strain model proposed by Thomsen et al.25 in which the laser-excited sample is assumed to develop instantaneous thermal stress of the form −3ββΔT(z), where B is the bulk modulus, β is the linear expansion coefficient, and ΔT(z) is the temperature profile along the sample depth (z). The finite coupling time between electrons and lattice can be accounted for by considering the following time dependent temperature profile

\[ ΔT(z,t) = \frac{(1 - R)F}{C_\delta} \left[ 1 - \exp(-t/\tau) \right] \exp(-z/\delta), \]

where R is the reflectivity, F is the incident fluence, C is the volumetric heat capacity, δ is the optical absorption depth, and τ is the electron–phonon coupling time constant. When the finite coupling time is introduced, the analytical expression for the strain propagation given by Thomsen et al. can no longer be used. Instead the strain propagation is calculated numerically. The numerical solution of the relevant equations of elasticity is presented in Fig. 3(a) in the form of a spatio-temporal map of the c-axis strain. Note the maximum strain of ~2.5% at the surface corresponding to a ~1000 K temperature change and a
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FIG. 2. (Color online) Rocking-curve differences taken at selected time delays relative to laser excitation at 26 mJ/cm². Two sets of measurements were taken: (a–f) grazing angle of 0.27° (below critical angle); (g–l) grazing angle of 0.5° (above critical angle). Open circles with error bars are experimental data points and solid lines are dynamical-diffraction calculations of a thermally strained crystal.

The spatio-temporal map of strain was used to create a deformed lattice structure of graphite and subsequently calculate the x-ray diffraction intensity of the deformed structure using dynamical diffraction theory performed on the Stepanov X-ray Server. The ~0.05° divergence of the x-ray beam was accounted for by performing simulations at different grazing angles and weight averaging the results according to a Gaussian distribution of angles. The 1.2% bandwidth of the x-ray beam was also accounted for by convoluting the weight-averaged result with a voigt lineshape. The calculated rocking curve for zero strain (unpumped sample) is shown as solid line in Fig. 1(b). Calculated rocking-curve differences at selected time points are shown as solid lines in Fig. 2(a–l). It is evident from the good agreement between measurements and calculations that the Thomsen model provides an accurate description of strain dynamics. Within our model we found the shape of the simulated rocking-curve differences to be sensitive to the optical absorption depth δ beyond a simple scaling factor. Therefore, we treated δ as a free-fit parameter and found the value of ~140 nm to best reproduce the measured rocking-curve differences. Note that this value of δ is within what has been observed experimentally.

IV. DISCUSSION

Qualitatively, the time-dependent features of the diffraction profiles can be understood as follows. Below critical angle, the x-ray absorption depth is less than the optical-absorption depth of ~140 nm. Strain is initially confined to the surface but evolves over time to mimic the laser-absorption profile. As strain waves propagate deeper into the material, more atomic layers become disturbed, but the average strain within the disturbed region is reduced. This is clearly seen by comparing the strain profiles at 50 ps and 100 ps in Fig. 3(b). With respect to x-ray diffraction, this simple picture explains both the increase in the intensity of the rocking-curve difference with time and the monotonic shift toward smaller angles of the zero crossing (intersection of rocking-curve difference and x-axis) indicating reduced strain. We note that at these shallow angles, strain estimated directly from the raw data as double the value of the zero crossing, agrees well with calculated...
strain. The maximum amount of shift of the 101 rocking curve of 0.16°, observed at +10 ps, corresponds to a c-axis expansion of 2.4%. Another interesting feature of the dynamics is the asymmetric character of the rocking-curve differences. This complex feature originates from the portion of the x-ray beam that by virtue of its large divergence penetrates deeper into the sample. Above critical angle the x-ray absorption depth is much larger than the optical-absorption depth. The rocking-curve difference for these measurements loses the character of a simple shift of a diffraction peak with conserved amplitude and width. For these measurements, strain cannot be directly extracted from the raw data. Nevertheless, employing dynamical-diffraction theory faithfully reproduces the observed features, as evident in Fig. 2(g–l).

A summary of the fluence-dependent measurements is shown in Fig. 4 in the form of surface strain at +50 ps as function of incident fluence. Note that the deviation from linearity is similar in character to the saturation of the atomic function of incident fluence. Note that the deviation from linearity is similar in character to the saturation of the atomic function of incident fluence. We have carried out additional simulations to set a limit on the lowest negative strain we can observe. Since the negative stress is short lived, it gives rise to strain confined to the topmost ∼5 nm of the sample. Given our surface sensitivity and the signal-to-noise ratio this negative strain component cannot be larger than 0.5% for the 26 mJ/cm² measurements.

FIG. 4. Measured strain at +50 ps for experiments conducted at different excitation fluences.

In conclusion our experiment supports the measurement of positive strains by Carbone et al. enforcing that these strains represent real structural dynamics. However, we disagree with the interpretation of the data suggesting that the observed strains point to a nonthermal contribution to the expansion of the lattice. To the contrary we believe that the saturation effect in the atomic displacements in our experiment and in Raman’s study indicate that the measured positive strains above 20 mJ/cm² are smaller than what is expected from thermal expansion. Finally this work demonstrates time-resolved x-ray diffraction in grazing geometry as a tool for resolving structural changes in light elements that do not efficiently scatter x rays. The new generation of light sources, with their superior beam qualities, will have sufficient surface sensitivity to fully explore the contraction effect that is thought to be limited to the topmost few layers in graphite.

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1jorgen.larsson@fysik.lth.se
26Note that the distance between the maxima and minima of the rocking curve difference is an incorrect measure of the rocking curve shift. This can be easily verified by considering the difference between two Gaussian curves of equal amplitudes and widths shifted by an amount that is much less than the width.