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CONDENSED MATTER

Direct Observation of the Generation of Coherent Optical Phonons in Thin Antimony Films by the Femtosecond Electron Diffraction Method

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The generation of coherent optical phonons in an antimony film has been directly observed by the femtosecond electron diffraction method. The sample has been excited by a femtosecond laser pulse ($\lambda = 800$ nm) and probed with a pulsed photoelectron beam. Oscillations of the intensity corresponding to vibration frequencies of optical phonons excited by the laser have been observed in the obtained diffraction patterns: totally symmetric (A_{1g}) and twofold degenerate (E_{2g}) phonon modes of antimony and their combinations.

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The determination of the characteristics of the structural dynamics of matter with a high space–time resolution is necessary in solid state physics, molecular physics, biology, and materials science (see reviews [1–4]). The time resolved electron diffraction (TRED) method proposed in [5] opened the possibility of studying the coherent structural dynamics of matter. An experimental breakthrough in the development of TRED was the usage of femtosecond laser pulses for the excitation of a sample and ultrashort photoelectron bunches synchronized with them for probing. This opened the possibility for the observation of the coherent dynamics of the nuclear subsystem of the studied sample [1–8].

The time resolution of the TRED method determined by the duration of electron pulses is the key parameter of experimental setups used for studying the coherent structural dynamics of matter [9]. It is known that the duration of a photoelectron pulse in the direct vicinity of a photocathode is equal to the duration of the pump laser pulse [10]. However, because of the Coulomb repulsion and the difference in the photoelectron velocities, ultrashort electron bunches moving from the photocathode to the sample are smeared near the target being probed. This circumstance determines smearing of the probing electron pulse by time-of-flight chromatic aberration [11]:

$$\Delta\tau_{eF} \approx \frac{\sqrt{2m_e\Delta E_e}}{eF},$$

where m_e is the mass of the electron, e is the elementary charge, ΔE_e is the spread of the initial kinetic energy of electrons, and F is the accelerating electric field strength. The Coulomb repulsion of photoelectrons in the bunch is another factor limiting the time resolution of the method [12]. The decrease in the trajectory of photoelectrons when using a femtosecond electron diffractometer makes it possible to reach a subpicosecond time resolution owing to the considerable increase in F and the decrease in the role of the Coulomb repulsion [13]. At the parameters $\Delta E_e \approx 0.4$ eV [8] and $F \approx 6.7 \times 10^6$ V/m, close to those used in our setup, the estimated value of $\Delta\tau_{eF}$ is ≈300 fs.

In this work, the generation of *coherent* optical phonons was observed for the first time using the TRED method with femtosecond time resolution. We note that the coherent optical phonons arising under the impact of a high-power ultrashort laser pulse on a solid has been studied for a quite long time by optical spectroscopy and X-ray diffraction methods, particularly in semimetals, where the efficiency of their generation is relatively large (see, e.g., [14–17] and references therein). The drawback of optical methods is that the wavelength of the probing radiation (~ 1 μm) is much larger than the characteristic sizes at which the variations of the crystal lattice (~10 pm) occur. Therefore, they cannot determine the absolute value of atomic displacements, though, according to the results of the comparison of the data of optical and X-ray measurements performed in [14], they ade-

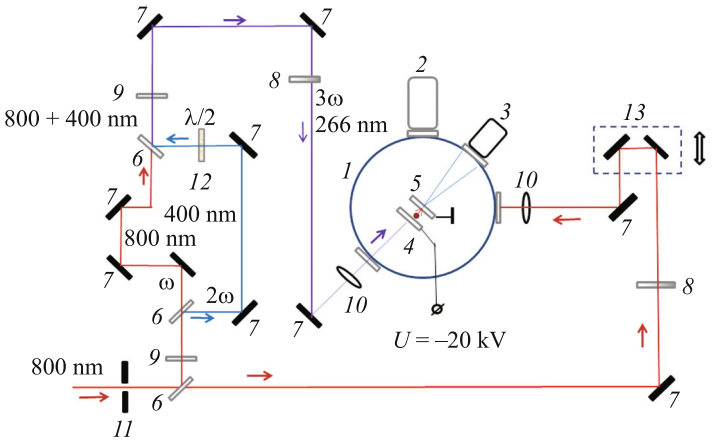

Fig. 1. (Color online) Experimental scheme: (*1*) vacuum chamber, (*2*) turbomolecular pump, (*3*) amplifier of the electron current on the basis of microchannel plates and CCD chamber, (*4*) silver photocathode, (*5*) anode + target, (*6*) beam splitters, (*7*) mirrors, (*8*) radiation attenuator, (*9*) converters into the second and third harmonics, (*10*) lenses, (*11*) diaphragm, (*12*) polarization rotator, and (*13*) delay line.

quately demonstrate the dynamics of coherent vibrations of atoms in the crystal lattice. In contrast to light, accelerated electrons (as well as X rays) make it possible to obtain information about the dynamics of the distribution function of internuclear distances, which is the Fourier image of the diffraction intensity [1–8], directly from the observed time-dependent diffraction pattern. The detection of the time behavior of the amplitude and shape of the diffraction maxima arising at electron probing makes it possible to determine the character of the motion of atoms within the unit cell under intense laser irradiation of the sample.

Electron probing has another advantage because the scattering cross section of fast electrons is four or five orders of magnitude larger than the scattering cross section of X rays [1, 2]. Therefore, electrons whose mean free path is many orders of magnitude less than that of X-ray photons can be used to probe thin samples, in particular, the optical-pulse-excited skin layer (~15 nm) of the antimony film studied in this work.

The space lattice of antimony refers to the rhombohedral system with two atoms in the cell A7 [18]. The structure of the complete representation of the vibrational modes of the structural type A7 has the form

$$\Gamma = A_{1g} + A_{1u} + E_g + E_u,$$

where A_{1g} and E_g are the optical modes active in the Raman spectra and A_{1u} and E_u are the acoustic modes. In this work, we report the first direct observation of the generation of *coherent optical* phonons in thin antimony films using the TRED method. To the best of our knowledge, only low-frequency *coherent acoustic* phonons in bismuth films were observed using this method in [19, 20].

The TRED method involves the optical pump–probe principle well known in spectroscopy, where the first pulse excites the sample and the second pulse applied with a tunable delay probes it. The scheme of the experimental setup used in our experiments and implementing the TRED method is shown in Fig. 1.

The main frequency of a femtosecond Ti:sapphire laser (λ_1 = 800 nm) was used as the pump beam and the photoelectron beam formed under the irradiation of the semitransparent photocathode with the third harmonic of the Ti:sapphire laser (λ_2 = 266 nm) was used as the probe beam. In this manner, the optical and photoelectron pulses were strictly synchronized. The laser pulse duration was 50 fs. The pulse repetition frequency was 1 kHz. The photocathode material was a silver layer with a thickness of ~30 nm deposited on a thin quartz plate. The studied sample was an antimony film with a thickness of about 30 nm prepared by thermal deposition in vacuum on a standard carbon substrate with a thickness of 20–30 nm used in transmission electron microscopes. The pump laser radiation was incident on the sample at an angle of 45°. The energy density in the laser beam on the sample surface was 1.5 mJ/cm^2. Such radiation energy density made it possible to perform rather long-term measurements without noticeable degradation of the sample. The kinetic energy of probe photoelectrons was 20 keV. The diameter of the electron beam in the region of the sample was ~0.1 mm. A lens based on a constant magnet adapted for the given energy of the electron beam served as a focusing system that made it possible to minimize the time-of-flight interval of electrons. The sample-diffracted electron beam amplified on the detector using microchannel plates got to the luminophore and was detected on a CCD camera.

Figure 2 shows a typical electron diffraction pattern of the studied antimony film obtained in the absence of optical excitation. The presence of bright reflections

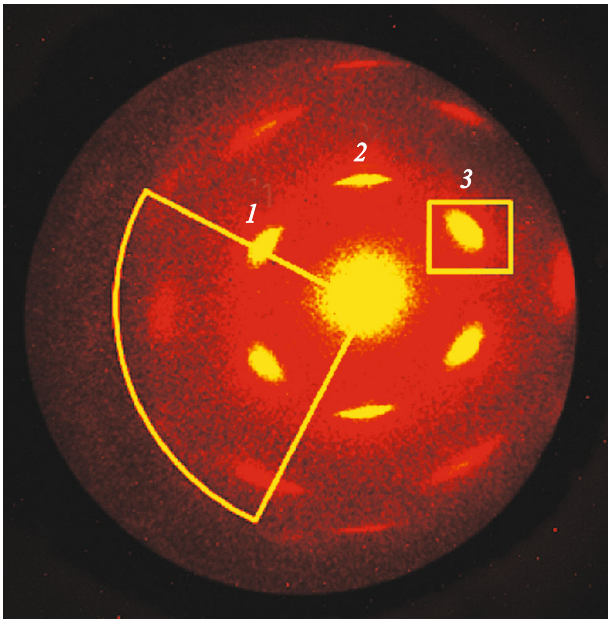

Fig. 2. (Color online) Electron diffraction pattern of the antimony films obtained using photoelectron pulse diffraction. The first, second, and third groups of reflections correspond to the (110), (300), and (220) planes, respectively. The rectangle and sector show the analyzed regions of the diffraction pattern.

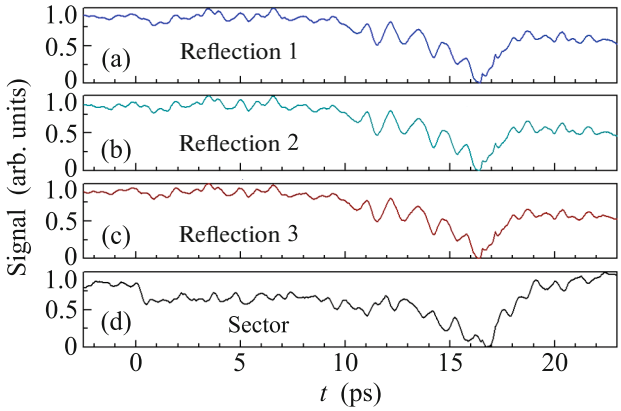

Fig. 3. (Color online) Normalized relative intensity of electron diffraction reflections in the antimony film versus the delay between the pump optical and probe photoelectron pulses. Panels (a)–(c) correspond to reflections *1*–*3*, respectively, in Fig. 2 and panel (d) is the sector signal.

unambiguously indicates the crystal (probably polycrystalline) nature of the studied sample.

The variation of the intensity of the diffraction pattern caused by the optical excitation of the sample was studied in the experiment as a function of the delay time between the pump and probe photoelectron pulses. The intensity of separate reflections *1*, *2*, and *3* and the integral signal in the sector shown in Fig. 2 were measured. Time scanning of the probe photoelectron pulse with respect to the pump femtosecond laser pulse was performed using a delay line with a step of 60 fs. The signal acquisition time at each step was 1 s. The intensity values measured in this manner were normalized to the intensity of the corresponding reflections in the absence of optical pumping. The results are shown in Fig. 3.

It can be seen that the dynamics observed in Fig. 3 is reproduced well at the detection in all studied regions of the diffraction pattern for the positive time delays corresponding to the arrival of the probe pulse after the pump one. At the excitation time, a sharp decay in the diffraction signal is observed, which is particularly distinct in Fig. 3d. The characteristic time of this decay is about 300 fs. A similar decay was observed in experiments on superfast electron diffraction in bismuth films in the *incoherent* response associated with the Debye–Waller effect owing to the increase in the rms stochastic displacement of atoms after the excitation of the sample [21, 22]. However, unlike the cited works, along with the rather complicated subsequent dynamics, one can separate the distinct oscillating component with the period on the order of a nanosecond reaching the maximum values and then relaxing in several picoseconds. The Fourier analysis (Fig. 4) showed that the observed signal modulation is due to the presence of four modes with frequencies of 1.1, 3.4, 4.6, and 6.4 THz, three of which were observed in [16, 17] in experiments on *optical probing* after the impact of a laser pulse with an energy density of ~1 mJ/cm^2 on an antimony sample. Following the attribution of the modes given in these works, it is possible to associate the frequencies of 4.6 and 3.4 THz with the totally symmetric (A_{1g}) and twofold degenerate (E_g) optical phonons of antimony and 1.1 THz with the difference optical vibration A_{1u}–E_g. The frequency of 6.4 THz for antimony in the time region was not observed earlier. It can be associated with the second harmonic E_g. We note that the pump laser pulse with a duration of 50 fs, the spectrum of which makes it possible to create phonons with frequencies to 7–8 THz, is responsible for the generation of coherent oscillations in our experiment.

The reliable detection of oscillations at the difference frequency with a period of about 1 ps (Fig. 3) makes it possible to state that the time resolution of the performed experiment determined by the electron pulse duration is close to the calculated value. Moreover, the usage of the small step (60 fs) at the time scanning of the photoelectron pulse with a duration of ≈300 fs allowed detecting the frequency of phonons of ≈6.4 THz. The relation of the coherent amplitudes of the main phonon modes and their overtones and/or combinations in our experiment differs from the data of the optical study of the coherent dynamics of the lattice, which can be due both to the specificity of the interaction between fast electrons and nuclei of the lattice and to the time resolution of our experiment. It

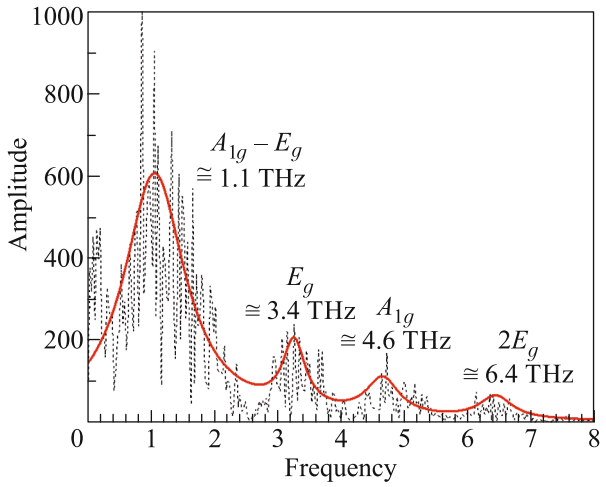

Fig. 4. (Color online) Fourier spectrum of laser-induced oscillations of the diffraction signal in the antimony film presented in Fig. 3. The dashed line shows the experimental data and the solid line is the Lorentzian fit to the peaks. The frequencies and attribution of the corresponding peaks are also presented.

should also be noted that the shape of the signal of coherent phonons in Fig. 3 differs noticeably from that observed earlier in experiments with optical probing [14–17] in the rather significant delay of their "excitation" with respect to the incoherent response. This effect can be explained by the same reasons as the delay of the appearance and the large amplitude of the incoherent signal of the vibrational modes from the surface as compared to the volume in thin bismuth films observed in [22]. At the same time, this problem needs further investigations.

To summarize, the generation of coherent optical phonons in a thin antimony film has been directly observed for the first time using superfast electron diffraction. These studies of the coherent dynamics of the antimony lattice indicate that a subpicosecond time resolution has been achieved. This is confirmed by the theoretical estimates and the direct observation of coherent optical phonon modes of antimony with the frequencies varying from 1 to 5–7 THz.

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