Thermal switching in the generation of photo-induced coherent phonon in bismuth

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Atomic motion of a photo-induced coherent phonon of bismuth (Bi) is directly observed with time-resolved x-ray diffraction under a cryogenic temperature. It is found that displacive excitation in a fully symmetric $A_{1g}$ phonon mode is suppressed at a temperature $T = 9$ K. This result implies a switching of the phonon-generation mechanism from displacive to impulsive excitation with decreasing the temperature. It is comprehensively understandable in a framework of stimulated Raman scattering. The suppression of displacive excitation also indicates that the adiabatic potential surface at the photo-excited state deviates from a parabolic one, which is assumed to be realized at room temperature. This study points out important aspects of phonon generation in transient phonon-induced quantum phenomena.

Controlling quantum phenomena in materials has been one of the central challenges in condensed matter physics. A well-promising technique is stimulating materials by external fields to excite into non-equilibrium states, where various exotic physical properties emerge. Optical pulses have been widely used as excitation sources to induce non-equilibrium quantum phenomena, such as ultrafast phase transitions, magnetic order transitions, and photo-induced superconductivities [1–3]. Since an ultrafast pulse triggers physical events in materials before reaching the thermal equilibrium, it has opened various non-equilibrium dynamics in the quantum phases that exist only at temperatures much lower than the ambient condition.

Photo-induced coherent phonon (14, 15) is one of the fundamental transient quantum phenomena in solids that promotes applications such as a conversion of phonon oscillations into coherent electromagnetic energy (1) and manipulation of atomic position and phonon to realize high-$T_c$ superconductivities (8–10). Understanding the nature of such coherent phonons has been indispensable to deal with these intriguing events. Over three decades, there have been a variety of experimental and theoretical studies to elucidate the generation mechanism in a wide temperature range and to reveal its relation with superconductivity (8–10) and squeezed states (11–13), for example. Bismuth (Bi) has been a model material for examining coherent phonon oscillations because it has a strong electron-lattice coupling. Two models, the impulsive stimulated Raman scattering (ISRS) model (14) and the displacive excitation of coherent phonons (DECP) model (15), are proposed to explain the generation mechanism of the coherent phonon in Bi. In the ISRS model, an ultrafast optical pulse having a broad energy spectrum impulsively induces stimulated Raman scattering resulting in atomic oscillations at the equilibrium position. In the DECP model, on the other hand, photo-excited carriers induce a shift of the equilibrium atomic position followed by atomic oscillations at the new position. These models deal with the atomic motion in Bi, however, the previous experimental studies with an optical pump-optical probe (OPOP) method have reported them indirectly through the data interpretation based on the electron-lattice interaction in Bi (5, 16–21). Due to a lack of direct data, the issue of what process is responsible for the phonon generation has remained controversial.

To examine this question, it is essentially important to directly observe the lattice dynamics on the femtosecond time scale using an x-ray free-electron laser (XFEL) [22, 23]. Furthermore, in dealing with the coherent phonon, it is required to cover its dynamical behavior over a wide temperature range. In this Letter, we report the first direct observation of the atomic motion of the photo-induced coherent phonon at a cryogenic temperature ($T = 9$ K). We performed time-resolved pump-probe x-ray diffraction (XRD) by using a newly developed instrument. Our results show that displacive excitation in the photo-induced coherent phonon of Bi is suppressed at low temperatures, implying a switching of the phonon-generation mechanism from displacive to impulsive excitation in a framework of stimulated Raman scattering.

A pump-probe XRD experiment was performed at BL3 of SACLA [24]. A 53-nm-thick Bi film epitaxially grown on a Si (111) substrate was excited with 800-nm optical laser pulses with a full-width-at-half-maximum (FWHM) duration of ~ 40 fs [26]. The photon energy $h\nu$ and pulse duration of the XFEL probe beam were 10 keV with a bandwidth of ~ 1 eV and ~ 7 fs (FWHM), respectively [27, 29]. The XFEL beam was focused to 100 $\mu$m in diameter (FWHM) with compound refractive lenses, while the optical laser was focused to 870 $\mu$m in diameter (FWHM). The angle between the optical laser and the XFEL beams was 1.8 degrees. The XFEL intensity of Bi 111 diffraction in a photo-excited state was detected with a multi-port charge-coupled device (MPCCD) as a function of the delay time of the XFEL pulse from...
The intensity variation of Bi 111 diffraction probes the $A_{1g}$ phonon mode oscillation along the [111] direction as shown in Fig. 1(a). The variation of the normalized diffraction intensity, $I(t)/I(0)$, caused by the atomic displacement along [111] direction, is represented by

$$\frac{I(t)}{I(0)} = \frac{|F_{111}(t)|^2}{|F_{111}(0)|^2} = \frac{\cos^2[3\pi x(t)]}{\cos^2[3\pi x(0)]}. \tag{2}$$

Figure 2(b) shows the fluence dependence of $x$ at $T = 9$ K obtained from the minimum values of the fitting curves to the non-oscillatory component around $t = 0$ shown in Fig. 2(b). For the low-temperature condition, the values of the non-oscillatory component with an exponential decay function convoluted with a Gaussian function. (c) Oscillatory component obtained by subtracting the non-oscillatory component from (b), shown as the blue circles. The black solid line represents a fitting curve using an exponential decay function convoluted with a Gaussian function.

To obtain the information on the $A_{1g}$ coherent phonon mode, we mainly fit the non-oscillatory component with an exponential decay function convoluted with a Gaussian function as shown in Fig. 2(b). We secondly obtain the oscillatory component by subtracting the non-oscillatory component from the total intensity variation as shown in Fig. 2(c). The frequency of photo-induced $A_{1g}$ coherent phonon mode is 2.95 THz at $T = 9$ K and the fluence of 1.6 mJ/cm$^2$ obtained from fitting with an exponentially decaying cosine curve. This result is almost consistent with the previous OPOP study [18].

We measured the fluence dependence at $T = 9$ K to investigate the difference in behavior between the low and room temperatures. Figure 2(a) shows the $A_{1g}$ phonon frequency as a function of fluence, which is compared with the published data measured at room temperature [32]. Although we observed a decrease in the phonon frequency as the fluence increases at $T = 9$ K as well as at room temperature [32], the reduction at $T = 9$ K is much smaller than that at room temperature. This behavior is consistent with the previous result obtained in the OPOP experiment [18].

We further investigate the atomic motion, which is inaccessible to the OPOP method, by analyzing the XRD data. The space group of Bi is #166 (R3m) and its structure factor for the $hkl$ Bragg diffraction, $F_{hkl}$, has the form

$$F_{hkl} = f_{Bi} \{ 1 + \exp [2\pi i (h + k + l) x] \} = 2f_{Bi} \exp [\pi i (h + k + l) x] \cos [\pi (h + k + l) x] \tag{1}$$

where $f_{Bi}$ is the atomic scattering factor for Bi, and $x$ is the atomic position in the trigonal unit cell along the [111] direction in a unit of the hexagonal unit-cell length, $c$, as shown in Fig. 1(a). The variation of the normalized 111 diffraction intensity, $I(t)/I(0)$, caused by the atomic displacement along [111] direction, is represented by

$$\frac{I(t)}{I(0)} = \frac{|F_{111}(t)|^2}{|F_{111}(0)|^2} = \frac{\cos^2[3\pi x(t)]}{\cos^2[3\pi x(0)]}. \tag{2}$$

Figure 2(b) shows the fluence dependence of $x$ at $T = 9$ K obtained from the minimum values of the fitting curves to the non-oscillatory component around $t = 0$ shown in Fig. 2(b). For the low-temperature condition, the values of the non-oscillatory component with an exponential decay function convoluted with a Gaussian function as shown in Fig. 2(b). The black solid line represents a fitting curve using an exponential decay function convoluted with a Gaussian function.

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FIG. 2. (a) Frequency of the A\textsubscript{1g} phonon mode of Bi obtained by fitting and (b) the atomic position \(x\) obtained from the variation of diffraction intensity around \(t = 0\) at \(T = 9\) K as a function of absorbed excitation fluence (blue circles), compared with those at room temperature reported by Ref. [32] (black squares). Error bars are 95% confidence intervals. The solid lines represent the values of \(x\) at the equilibrium position before a photo-excitation used in this work (blue) and Ref. [32] (black). The dashed lines are guides to the eye. The arrows indicate examples of \(\Delta x\) at \(T = 9\) K (blue) and room temperature (black).

of \(x\) and \(c\) before a photo-excitation were 0.46814 and 11.797 Å, respectively [32]. The crystal structure of Bi is a result of Peierls distortion from a high-symmetry cubic structure. This distortion deviates \(x\) from 0.5 of the cubic structure. The decrease of the diffraction intensity shown in Fig. 1(b) indicates that quasi-equilibrium atomic position moves toward \(x = 0.5\) because the 111 diffraction is forbidden for \(x = 0.5\) [32]. As the fluence increases, \(x\) gradually increases toward \(x = 0.5\), which implies the Peierls distortion decreases. However, the magnitude of the deviation of \(x\) from the equilibrium point, i.e. \(\Delta x = x - x(0)\), observed at \(T = 9\) K is significantly smaller than that observed at room temperature [32], as shown in Fig. 2(b). This result is consistent with the small change in the phonon frequency as the fluence increases at \(T = 9\) K [Fig. 2(a)] [32].

In the following, we show that the small deviation \(\Delta x\) at \(T = 9\) K observed in this study plays a key role in determining the phonon-generation mechanism. First, we note that the deviation corresponds to the fully symmetric A\textsubscript{1g} phonon mode, which has been observed predominantly at room temperature. The generation of this mode was explained by the DECP model [15]. Therefore, the small value of \(\Delta x\) implies that displacive excitation in the A\textsubscript{1g} phonon mode is suppressed at low temperatures. In the meanwhile, there is another mode of photo-induced coherent phonon, the doubly degenerate E\textsubscript{g} phonon mode, where atoms move in the directions perpendicular to [111] [Fig. 1(a)] [19–21, 31]. The E\textsubscript{g} phonon generation was explained by the ISRS model [14]. In the literature, the E\textsubscript{g} phonon mode was reported to be generated at low temperatures [14, 21, 31]. This is ascribed to impulsive excitation, which is considered to play a more influential role as the temperature is decreased. Furthermore, the previous OPOP and spontaneous Raman scattering measurements [21] concluded that the DECP and ISRS mechanisms contribute comparably even in the A\textsubscript{1g} phonon mode at low temperatures.

In this context, our temperature-dependent data shows switching of the A\textsubscript{1g} phonon-generation mechanism from DECP to ISRS with decreasing the temperature. The switching can be given a physical interpretation when using the theoretical model reported by Stevens et al. [34]. Stimulated Raman scattering was described therein by two tensors, consisting of a common real component but different imaginary components. If the imaginary (real) part dominates, the generation mechanism of the photo-induced coherent phonon is displacive (impulsive). Therefore, one can interpret our measurement in terms of the temperature-dependent imaginary component when one assumes that the essence of photo-induced coherent phonon generation in Bi is the stimulated Raman scattering process. The imaginary component, which contributes to the displacive driving force, is proportional

![Graph](image-url)

FIG. 3. Im(\(\epsilon\))/(\(\hbar\omega\)) of the A\textsubscript{1g} phonon mode of Bi as a function of absorbed excitation fluence at \(T = 9\) K (blue circles) and room temperature (black squares) using the values in Fig. 2(a). The dashed lines are guides to the eye.
However, this conventional model is unlikely under the present pumping condition of semimetal Bi at low temperatures. Since there is no significant change in the crystal structure of Bi, the shape of the potential surface also should not change significantly with temperature. Thus, it is reasonable to consider that the potential shape of the ground state is parabolic, regardless of temperature, while that of the excited state is non-parabolic. As shown in Fig. 4 we propose a possible potential energy surface at the photo-excited state, which has multiple local minima mutually displaced in the [111] direction. When \( k_B T \) is smaller than the potential barrier between two minima, \( \Delta_p \), the atomic displacement settles at the local minimum. This picture can explain the temperature-dependent behavior of \( x \) or the suppression of displacive excitation at low temperatures. Our experimental result at \( T = 9 \) K implies that \( \Delta_p \) is as small as \( k_B T = 0.78 \) meV and it can be neglected when the thermal broadening of the Fermi-Dirac function becomes as large as \( k_B T = 26 \) meV at room temperature. Thus, the potential surface at the excited state appears as a single minimum at room temperature, as reported in the previous study [32].

In conclusion, we directly observed the suppression of displacive excitation in the photo-induced \( A_{1g} \) coherent phonon mode of Bi at \( T = 9 \) K. The result implies the thermal switching of the excitation process from DECP to ISRS. It can be corroborated by the temperature dependence of the imaginary component of tensor, which describes stimulated Raman scattering. Furthermore, the suppression of atomic displacement indicates that the potential surface in Bi at the photo-excited state could be more complex than the parabolic one at the ground state. Our experimental discovery and the phenomenological model become the research targets for the future development of theoretical studies. Understanding the generation mechanism of the coherent phonon will lead to control phonons using light, which could enable us to create new quantum phenomena [36]. Our results open up an avenue for the investigation of transient phonon-induced phenomena on not only semimetals and semiconductors but also high-\( T_c \) superconductors [8–10, 36].

This experiment was performed at BL3 of SACLA with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2020A8070). The synchrotron radiation experiments were performed to develop and evaluate the equipment at BL19LXU in SPring-8 with the approval of RIKEN (Proposal No. 20190042). We thank Dr. Suguru Ito for the sample preparation, and Dr. Jun Haruyama and Dr. Takeshi Suzuki for the valuable discussion.

FIG. 4. (a) Schematic of the possible potential surfaces of Bi at low temperatures for ground and photo-excited states. (b) Slices of the possible potential surfaces along the [111] axis. The red arrow indicates the transition of the atoms from the ground to the photo-excited energy surface.

to \( \text{Im}(\varepsilon)/\Omega \), where \( \varepsilon \) is the dielectric function, and \( \Omega \) is the phonon frequency [34]. Figure 3 shows fluence dependence of \( \text{Im}(\varepsilon)/\Omega \) at \( T = 9 \) K and room temperature using the values of \( \Omega \) shown in Fig. 2(a). The experimental values of \( \text{Im}(\varepsilon) \) reported by Hunderi [35] were used. Although the values of \( \text{Im}(\varepsilon)/\Omega \) at \( T = 9 \) K and room temperature are comparable in the small fluence region, the values at \( T = 9 \) K are smaller than those at room temperature in the high fluence region (\( > 1 \) mJ/cm\(^2\)). This is attributable to the fact that \( \Omega \) at low temperatures is larger and its smaller change as the fluence increases than those at room temperature, as shown in Fig. 2(a) and the previous OPOP studies [10, 18, 20, 21]. This result suggests that high phonon frequency is equivalent to the small driving force of DECP at low temperatures, which results in the small variation of \( \Delta x \). Furthermore, from the previous study showing that the electron-phonon coupling of the \( E_g \) phonon mode becomes stronger at low temperatures than that at room temperature [21], one can expect redistribution of excitation energy from the \( A_{1g} \) to the \( E_g \) mode.

The small value of \( \Delta x \) apparently suggests that excited carriers do not induce an apparent change in the adiabatic potential surface. As long as the optical transition is considered between the parabolic potentials in \( x < 0.5 \), the small change in the potential surface can be explained only by a decrease in the carrier density [20, 32]. However, this conventional model is unlikely under the

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