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Origin of coherent phonons in Bi$_2$Te$_3$ excited by ultrafast laser pulses

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Femtosecond laser pulses are used to excite coherent optical phonons in single crystal Bi$_2$Te$_3$ thin films. Oscillations from low- and high-frequency A$_{1g}$ phonon modes are observed. A perturbation model based on molecular dynamics reveals various possibilities of phonon generation due to complex interactions among different phonon modes. In order to elucidate the process of phonon generation, measurements on thin films with thicknesses below the optical absorption depth are carried out, showing that a gradient force is necessary to excite the observed A$_{1g}$ phonon modes, which provides a refined picture of displacive excitation of coherent phonon.

In this paper, we employ femtosecond time-resolved phonon spectroscopy to investigate coherent phonon dynamics in single-crystal Bi$_2$Te$_3$ thin films. Excitation of low- and high-frequency optical phonons is observed. A perturbation model based on molecular dynamic (MD) simulation is developed to explain the interactions among the phonon modes. The combined MD studies and the phonon spectroscopy on single-crystal films with thicknesses ranging from a few nm to hundreds of nm reveal phonon interactions and the driving forces for coherent phonon excitation.

All experiments were performed in a collinear two-color (400 nm and 800 nm) pump-probe scheme. The laser pulses have 100 fs full width at half maximum pulse width, 800 nm center wavelength, and repetition rate of 5 kHz. A second harmonic crystal is used to generate pump pulses at 400 nm. The pump and the probe beams are focused onto the sample at normal direction with diameters of 80 and 20 μm and fluence of about 0.25 mJ/cm$^2$ and 0.02 mJ/cm$^2$, respectively. The samples are c-plane oriented single crystalline Bi$_2$Te$_3$ thin films grown via metal-organic chemical-vapor deposition on GaAs (100) substrates. The penetration depths for 400 nm and 800 nm are about 9.1 nm and 10.0 nm calculated by data in (Ref. 21), so the entire excited region is probed. We also tested using an 800-nm pump and a 720-nm probe, which led to similar results. The thickness of the samples ranges from 1.0 μm to 5 nm.

Bulk Bi$_2$Te$_3$ has a rhombohedral primitive cell in space group R$3\bar{m}$, and the corresponding conventional unit cell is hexagonal, consisting of periodically arranged fivefold stacks along the $c$ axis: TeI–Bi–TeII–Bi–TeI. The five atoms in each primitive unit cell give three acoustic phonon modes and twelve optical phonon modes. The twelve optical modes are two $A_{1u}$ and two $E_u$ (Raman active), and two $A_{1u}$ and two $E_u$ (IR active). Only eight modes are counted here due to the degeneracy of the transverse modes. Figure 1 illustrates the corresponding atomic displacements for these modes. For MD simulations, we employ two-body potentials that are derived from the density-functional theory and have been implemented in MD to calculate the bulk lattice.
thermal conductivity\textsuperscript{23} and the mode-wise lattice thermal conductivity.\textsuperscript{24} The two-body potential is used together with the Wolf’s summation\textsuperscript{25} to evaluate the long-range Coulomb conductivity.\textsuperscript{24} The two-body potential is used together with the interatomic potentials, which reflects the phonon interactions among different phonon modes. Figures 3(a) and 3(b) show the transient atomic displacements of TeI atoms for excitation of $A_{1g}$ phonons are about 12 ps and $A_{2g}$ phonon is much shorter, 0.72 ps. The possible reasons for stronger phonon damping observed experimentally are that more than one mode can be excited (see below) and also the existence of defects in the sample.

We now analyze the possible processes that drive phonon oscillations, specifically, the ponderomotive force, the thermal force, and the polarization force.\textsuperscript{19} Since our sample has its $c$ axis perpendicular to the sample surface, the ponderomotive force and the thermal force that originate from the electric

![FIG. 1. Optical phonon modes in Bi$_2$Te$_3$.](image)

![FIG. 2. Coherent phonons excited by femtosecond laser pulses (dots) in the 1-$\mu$m-thick Bi$_2$Te$_3$ film and the fitting result (solid line).](image)

![TABLE I. Comparison of phonon frequencies from Raman and IR spectroscopy, femtosecond time-resolved spectroscopy, and MD simulation. All units are in THz.](table)

\begin{tabular}{|c|c|c|c|}
\hline
Mode & Raman (Refs. 22 and 27) & IR (Ref. 22) & Femtosecond spectroscopy \& MD simulation \\
\hline
$A_{1g}$ & 1.88 & 1.82 & 1.84 \\
$A_{2u}$ & 4.02 & 3.91 & 3.74 \\
$A_{1u}$ & 2.82 & 2.88 & \\
$A_{2u}$ & 3.60 & 3.58 & \\
$E_{1g}$ & 1.1 & 1.47 & \\
$E_{2g}$ & 3.09 & 3.42 & \\
$E_{1u}$ & 1.50 & 1.43 & \\
$E_{2u}$ & 2.85 & 2.90 & \\
\hline
\end{tabular}
FIELD GRADIENT AND TEMPERATURE GRADIENT ALONG THE c AXIS CAN BE RESPONSIBLE FOR GENERATING THE LONGITUDINAL A1\(_{ig}\) AND A2\(_{ig}\) PHONONS. THE PONDEROMOTIVE FORCE AND THE THERMAL FORCE CAN BE ESTIMATED AS:

\[
\begin{align*}
    f_{\text{pond}} & \approx \frac{\varepsilon_D - 1}{\varepsilon_D} \frac{I}{c}, \\
    f_{\text{thermal}} & \approx \frac{n_e k_B T_{e', \text{max}}}{\delta_s}.
\end{align*}
\] (2)

For Bi\(_2\)Te\(_3\), the Drude-type cross-plane dielectric constant \(\varepsilon_D\) is 12.81, calculated from the dielectric constant, and the penetration depth is about 9.1 nm for the excitation wavelength of 400 nm. \(c\) is the speed of light, and \(k_B\) is the Boltzmann constant. The peak laser intensity is estimated as \(I = F/t_p\), where \(F\) is the laser fluence and \(t_p\) is the pulse width (0.25 ml/cm\(^2\) and 100 fs). The hot electron density is estimated as \(n_e = \alpha F/(\Delta E \delta_s)\), where \(\alpha\) is the absorptivity (0.31 at 400 nm) and \(\Delta E\) is the bandgap [0.15 eV for Bi\(_2\)Te\(_3\) (see Ref. 21)]. Here avalanche excitation of electrons is assumed since the photon energy (3.1 eV) is much larger than the band gap. The value of \(n_e\) is determined to be \(3.55 \times 10^{27} \text{ m}^{-3}\), which is then used to evaluate the Fermi energy of the excited electrons, \(\varepsilon_F = \hbar^2/(3\pi^2 n_e)^{2/3}/(2m)\) (see Ref. 28), where \(m\) is the mass of electrons and \(\hbar\) is the reduced Planck’s constant. The value of \(\varepsilon_F\) is calculated to be 0.85 eV. The specific heat of the excited electrons is calculated as \(c_v = \pi^2 k_B^2 T_c n_e/(2\varepsilon_F)\), where \(T_c\) is the electron temperature. The absorbed energy density by electrons is \(\alpha F/\delta_s = \int_{T_0}^{T_{e', \text{max}}} c_v dT\), where \(T_{e', \text{max}}\) and \(T_0\) are the maximum temperature and the initial temperature, respectively. The maximum electron temperature \(T_{e', \text{max}}\) is then estimated as \(T_{e', \text{max}} = [4\varepsilon_F \alpha F/(\pi^2 n_e \delta_s)]^{1/2}/k_B\), where \(T_{e', \text{max}}\) is assumed to be much higher than \(T_0\) and \(T_{e', \text{max}}\).
FIG. 4. (a) Coherent phonons in Bi$_2$Te$_3$ thin films with different thicknesses. (b) Coherent phonon amplitude versus the Bi$_2$Te$_3$ film thickness, obtained by fitting with a damped oscillator. (c) Raman spectra of Bi$_2$Te$_3$ thin films with different thicknesses. The three peaks are 62 cm$^{-1}$ (1.86 THz), 102 cm$^{-1}$ (3.06 THz), and 132 cm$^{-1}$ (3.96 THz) for the A$_{1g}$, the E$_g$, and the A$_{2g}$ modes. (d) Pump-probe signal of 10-nm-thick Bi$_2$Te$_3$ thin film illuminated by 30$^\circ$ incident pump beam.

is determined to be 2636 K. It is then found from Eq. (2) that in our case, the thermal force $f_{\text{thermal}} = 1.42 \times 10^{16}$N/m$^3$ dominates at the end of pump pulse, which is about two orders of magnitude higher than the ponderomotive force, $f_{\text{pond}} = 1.08 \times 10^{14}$N/m$^3$.

Both the thermal force and the ponderomotive force are gradient force, as they depend on either a thermal gradient or an electric-field gradient. On the other hand, we note that the gradient force does not produce the exact motion on Bi or Te ions of the A$_{1g}$ or the A$_{2g}$ mode as depicted in Fig. 1(a), rather, it produces a combination of the motions of the two modes. This indicates that these two modes can be excited simultaneously, which agrees with the experimental observation that there is no time delay between generations of the two phonon modes.

In our experiments, transverse phonons, which can be generated by the polarization force, are not observed since anisotropic detection$^{29}$ is not implemented. It is possible that the transverse modes are also generated but decay into the observed longitudinal phonons quickly. For example, the lifetime of the E$_g$ mode is found to be short in Bi.$^{30}$ In addition, the excited carrier density in our case is similar to that used for Bi where strong phonon-phonon interaction is predicted.$^{5,31}$ The MD calculations also show that it is indeed possible that transverse phonons can generate longitudinal phonon modes. Figure 3(e) shows the phonon spectra if the initial excitation is the E$_g$ mode. In this case, both A$_{1g}$ and A$_{2g}$ phonons are also generated. In addition, due to the asymmetrical Bi$_2$Te$_3$ lattice structure, the polarization force can directly excite the longitudinal phonon modes. The polarization force can be estimated as:$^{19}$

$$f_{\text{polarization}} \approx \frac{4\pi \chi_0 I}{d^3},$$

where $\chi_0 \approx (\varepsilon_D - 1)/4\pi$ (see Ref. 32), and $d$ is the averaged nearest-neighbor distance ($\sim 3.33$ Å for Bi$_2$Te$_3$). The polarization force is estimated to be about $2.96 \times 10^{15}$N/m$^3$, larger than the ponderomotive force but smaller than the thermal force.

To evaluate the possibility that the observed A$_{1g}$ modes are generated by initially excited E$_g$ phonons or directly excited by the polarization force, experiments were carried out on samples with thinner thicknesses, from 100 nm to 5 nm. It is seen from Fig. 4(a) that while the oscillations in 100- and 50-nm-thick films have similar amplitudes (also similar to the 1-$\mu$m film), the amplitude of coherent phonon decreases significantly when the film thickness decreases, and no coherent phonons can be observed when the thickness is 10 nm [Fig. 4(b)]. We verified that the thinner films still have crystalline structure, as shown in the Raman scattering data in Fig. 4(c). The widths of the Raman peaks in the thinner films are slightly wider, indicating longer interatomic distances or larger tensile stress and stronger anharmonicity in thinner films. The band gap in
the very thin Bi$_2$Te$_3$ films can be wider, for example, $\sim 0.25$ eV in 5-nm-thick films compared with 0.15 eV in bulk, but still much smaller than the laser photon energy, so the light absorption process is still interband transition.

We attribute the sharp decrease of the phonon oscillations in 10-nm and 5-nm films to the lack of gradient force driving the phonon generation. This is because the optical absorption depth in Bi$_2$Te$_3$ is 9.1 nm at 400 nm wavelength. These result in a nearly uniform electric field across a thickness less than 10 nm. We also irradiate the pump pulse at an inclined angle with respect to the sample surface. The polarization force thus has a component along the $c$ axis of the Bi$_2$Te$_3$ crystal. Figure 4(d) shows that similar to the results in Fig. 4(a), no coherent phonon oscillation is observed. This indicates that the polarization force is not sufficient to generate the observed longitudinal phonon modes. Therefore, we conclude that the longitudinal phonon modes observed in the experiments are not decayed from the $E_2$ mode excitation or directly excited by the polarization force. An additional observation from Fig. 4(a) is that there is a large amplitude, slow varying oscillations with period of 20 ps, regardless of the film thickness. These oscillations are driven by gradient forces such as thermal force, which provides a refined picture of phonon generation process within DECP.

In summary, we studied the coherent phonon dynamics in Bi$_2$Te$_3$ using ultrafast phonon spectroscopy and perturbation-based MD simulations. Complex features observed in phonon spectroscopy were determined to be the A$_{ig}$ and the A$_{ig}$ longitudinal phonon modes. Using thin films with thicknesses comparable or less than the optical absorption depth in combination with the MD analyses, it was found that the A$_{ig}$ phonons were driven by gradient forces such as thermal force, which provides a refined picture of phonon generation process within DECP.

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