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Phys. Rev. B **96**, 134302 — Published 6 October 2017

DOI: [10.1103/PhysRevB.96.134302](https://doi.org/10.1103/PhysRevB.96.134302)

Coherent Control of Optical Phonons in Bismuth

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(Dated: September 22, 2017)

We have conducted degenerate pump-pump-probe experiments on semimetal bismuth with femtosecond time resolution, varying both pump-probe and inter-pump time delays. The observed phonon dynamics, including the amplitude, damping, frequency, and phase, can be modeled by the interference of two chirped damped oscillators. No lattice anharmonicity along the trigonal axis is observed. We also find evidence for phonon-mediated relaxation of energy density at the sample surface.

PACS numbers: 63.20.Ry, 78.47.jg, 78.66.Bz

I. INTRODUCTION

The development of femtosecond laser technology has enabled direct time-domain study of ultrafast material dynamics. Since energy can be deposited on a timescale shorter than the characteristic molecular and atomic motions, unique phenomena such as coherent phonon oscillations can be observed in a multitude of systems¹⁻³. The semimetal bismuth has been of particular interest for the study of coherent phonon physics. Many of bismuth's unique features arise from its characteristic Peierls-like distortion. The crystal structure of bismuth is rhombohedral, with two atoms per unit cell rather than a higher-symmetry cubic structure. The distortion along the trigonal axis opens a gap at the T point in the Brillouin zone, lowering the overall electronic energy which compensates for the increase in lattice energy. This structural distortion results in a bismuth atom equilibrium position that is sensitive to electronic excitation. When optical excitation promotes carriers into higher energy states, the equilibrium position of the bismuth atoms shifts toward the symmetric phase, reducing the Peierls distortion⁴. In terms of the model of displacive excitation of coherent phonons (DECP)⁵, the sudden displacement in equilibrium position directly launches coherent A_{1g} optical phonon oscillations, which correspond to pairs of bismuth atoms oscillating about their new equilibrium positions along the trigonal axis. The coherent A_{1g} lattice displacement induces a change in dielectric susceptibility via the diagonal elements of the Raman tensor³, which can be observed in transient reflectivity measurements. According to density functional theory (DFT) calculations and experiments^{4,6}, the curvature of the potential energy surface also depends on the excited carrier density, leading to a phonon frequency that red-shifts with increasing pump fluence (electronic bond softening). This bond softening gradually lessens as carriers relax or diffuse, resulting in chirped phonon oscillations.

When bismuth is excited by two pump pulses with a small delay between them, the coherent phonon amplitude can be varied with surface carrier concentration and lattice temperature approximately fixed. Therefore, one can investigate the lattice dynamics that result from large-amplitude phonon motions independent

of electronic or thermal contributions. Although excitation of bismuth with a pair of optical pump pulses has been probed experimentally several times in the literature^{4,7-13}, almost none have fine inter-pump delay steps and a long delay window in the inter-pump delay due to the time-intensive nature of performing a two-dimensional pump-probe measurement. With single-shot spectroscopy, we can acquire a pump-probe trace with one laser shot and thus reduce the dimension of delay scan down to one. In this paper, we demonstrate coherently controlled phonon dynamics with four representative fluence settings, and we construct an interference model based on two oscillators that can reproduce the observed phonon oscillations.

II. METHOD

The single-shot setup is shown in Fig. 1 and more details can be found in the reference¹⁴. The light source is a commercial Ti:sapphire regenerative amplifier system with a central wavelength of 800 nm, which produces 60 fs pulses with 3 mJ pulse energy at a repetition rate of 1 kHz. The output of the laser is down-counted by a pulse picker for use in single-shot detection. The pump arm is essentially a Michelson interferometer, providing collinear pairs of excitation pulses whose inter-pump delay is scanned by a linear motorized stage. The probe beam passes through two crossed echelons to create a 20×20 two-dimensional temporal array corresponding to a 9.3 ps observation window with 400 delay points. The pump beams and probe beamlets are then focused on the sample surface with spot sizes of $600 \mu\text{m}$ and $200 \mu\text{m}$ respectively. The sample, a 300 nm thick polycrystalline bismuth film sputtered onto a glass substrate, is kept at 80 K to exploit the longer phonon lifetimes and higher damage threshold at reduced temperatures. The signal probe, which is reflected off the sample, as well as the reference probe, which bypasses the sample, are both projected onto a CCD camera, forming an image of two 20×20 grids. A single-shot trace can then be extracted from a pump-on image and a pump-off image by binning and unfolding the data encoded onto the grids. With this balancing technique, the laser fluctua-

FIG. 1. A schematic of the dual-echelon single-shot pump-probe setup. BS, beamsplitter; PBS, polarization beamsplitter; HWP, half-wave plate; ND, neutral-density filter; LED, light-emitting diode; CCD, charge-coupled device.

tions and the inhomogeneities in the beam profile can be substantially compensated. The two pumps are polarized parallel to each other and orthogonal to the probe polarization so that pump scattering can be removed by a polarizer. To enhance the signal-to-noise ratio, 100 shots are applied in the acquisition of each transient reflectivity trace. The single-shot method has been used for ultrafast measurements on samples that are damaged or undergo permanent change induced by the pump pulses^{15,16}, but in the present measurements we were well below the damage threshold. The single-pulse method was exploited to avoid the need for scanning of two independent time axes.

III. RESULTS

Fig. 2 shows one set of experimental data and other datasets are shown in the supplementary materials^{17,18}. The two-dimensional fast Fourier transform (2D FFT) spectrum of this set of traces is shown in Fig. 3. For simple illustrative purposes, we denote the many-electron state with carriers promoted by pump 1 as the first electronic excited state and the many-electron state with carriers promoted by both pumps as the second electronic excited state. The first pump pulse promotes the system from the ground state into the first electronic excited state and creates a vibrational wavepacket. The 2D spectral peak at ($\nu_t = 2.8$ THz, $\nu_\tau = 3.0$ THz) corresponds to the wavepacket whose frequency is 3.0 THz after excitation by pump 1 and is red-shifted to 2.8 THz after excitation by pump 2. The peak at (2.8 THz, 0) is another wavepacket generated by pump 2 from the first electronic excited state due to the shift of the potential and is independent of the wavepacket induced by pump 1. The coherent lattice response that we measure after both excitation pulses is the superposition of the displacements of these two wavepackets. If the two wavepackets oscillate at the same frequency, the composite motion can be treated as a single wavepacket in the

FIG. 2. (a) The transient reflectivity of bismuth under double pump excitation as a function of pump-pump delay, τ , and pump-probe delay, t . Pump fluences are 0.6 and 0.5 mJ/cm². (b) Individual transient reflectivity traces along with their fits at various values of the pump-pump delay τ .

second electronic excited state. It will be shown later on that this single-oscillator description fails to adequately explain the obtained data. Lastly, the peak at (0, 3.0 THz) (and the nearby ripples) is rather unexpected in that it suggests a modulation of the equilibrium position of the potential surface or the carrier density by the coherent phonon oscillations. Note the peak at (0, -3.0 THz) is simply a mirror of the peak at (0, 3.0 THz) due to the 2D FFT.

In the time domain, we fit the transient reflectivity trace following the second pump to a chirped damped harmonic oscillation and two monotonic decays plus a DC term:

$$\frac{\Delta R}{R} = \sigma_1 e^{-\Gamma_1 t} + \sigma_2 e^{-\Gamma_2 t} + \sigma_3 + A e^{-\Gamma_p t} \cos[(\omega_0 - \Delta\omega_p e^{-\Gamma t})t + \phi_p]. \quad (1)$$

The unexcited A_{1g} phonon frequency $\omega_0/2\pi$ is 3.03 THz at 80 K¹⁹ and the initial phonon frequency after excitation is $\nu_p = (\omega_0 - \Delta\omega_p)/2\pi$. In our fluence range, two exponential decays provide better fits than a single exponential term^{11,20}. The fitted results of four measurements

FIG. 3. The 2D FFT spectrum of the transient reflectivity data found in Fig. 2(a) for $t > 0$. The x-axis represents the Fourier conjugate of the pump-probe delay, ν_t , and the y-axis represents the Fourier conjugate of the pump-pump delay, ν_τ . The maximal intensity at origin (0, 0) is normalized to 100.

TABLE I. Fixed parameters used in fitting the transient reflectivity traces to damped chirped oscillators with two monotonic decays.

Pump 1 Fluence (mJ/cm ²)	Pump 2 Fluence (mJ/cm ²)	Γ_1 (ps ⁻¹)	Γ_2 (ps ⁻¹)	Γ (ps ⁻¹)
0.6	0.5	2.00	0.26	0.08
3.1	0.6	1.00	0.11	0.09
0.3	3.4	1.90	0.24	0.19
3.1	3.4	1.22	0.15	0.30

with different fluences are shown in Fig. 4. In each fitting process, we assume the relaxation constants Γ_1 , Γ_2 , and Γ are not functions of the pump-pump delay in order to avoid crosstalk between parameters. Those constants are listed in Table I.

As expected, the amplitude and phase of the phonon oscillations can be coherently controlled by varying the pump-pump delay. When pump 1 is much stronger than pump 2, the composite response will be dominated by the oscillation initiated by pump 1 and only weakly modulated by pump 2. In this case, we find a strong decay in the phonon amplitude due to the damping of phonon 1 while the phase grows monotonically with inter-pump delay. On the other hand, if pump 2 is much stronger, the phonon amplitude is nearly constant and the phase

is also weakly varying. When the fluences of the two pumps are roughly equal, there will be a strong modulation in both amplitude and phase. By carefully tuning the inter-pump delay and the fluences, nearly complete cancellation of A_{1g} mode is possible and the E_g mode, whose amplitude is more than 10 times smaller than the A_{1g} amplitude²¹, can be observed¹⁷.

We also compare the phonon oscillations induced by pump 1 alone with the estimated position $A \cos \phi_p$ from the fitting of the rest of the trace after pump 2 arrives. The two positions agree very well at low fluences. The deviation at high fluences indicates that the phonon displacements move far enough toward the high-symmetry unit cell configuration that a nonlinear dependence of reflectivity on phonon displacement or lattice anharmonicity may occur. In the high-symmetry configuration, the phonon mode is Raman-inactive, *i.e.* there is no change in the complex refractive index (or the reflectivity) for infinitesimal phonon displacements about the high-symmetry configuration since displacements in opposite directions must have the same effects.

The strong modulation in the phonon damping along with its unintuitive sawtooth shape indicate that the results at hand cannot be adequately modelled by a semi-classical picture of a single oscillating bismuth lattice wavepacket. As suggested by the 2D spectrum, the phonon dynamics can be modelled by the superposition of two chirped and damped oscillators. The otherwise unexplained modulation in observed damping appears when the phase difference of the two oscillators depends not only on the inter-pump delay, τ , but the elapsed time, t , as well. If we ignore the sine term from the DECP mechanism⁵, the two-oscillator can be modeled as:

$$\begin{aligned}
 Q_1 &= A_1 \{ e^{-\Gamma_{e1}\tau - \Gamma_{e2}t} \\
 &\quad - e^{-\Gamma_{p1}\tau - \Gamma_{p2}t} \cos[\omega_1\tau + \omega_2t + \phi(t)] \}, \\
 Q_2 &= A_2 \{ e^{-\Gamma_{e2}t} - e^{-\Gamma_{p2}t} \cos \omega_2t \}.
 \end{aligned} \tag{2}$$

where $A_1(A_2)$ is the phonon amplitude excited by pump 1(2). $\Gamma_{p1}(\Gamma_{p2})$ is the phonon damping constant after pump 1(2) arrives. The chirped phonon frequencies can be modeled as

$$\begin{aligned}
 \omega_1 &= \omega_0 - \Delta\omega_1 e^{-\Gamma_{e1}\tau}, \\
 \omega_2 &= \omega_0 - (\Delta\omega_1 e^{-\Gamma_{e1}\tau} + \Delta\omega_2) e^{-\Gamma_{e2}t}.
 \end{aligned} \tag{3}$$

where $\omega_0/2\pi$ is the unexcited phonon frequency 3.03 THz, $\Delta\omega_1(\Delta\omega_2)$ is the amount of electronic softening, and $\Gamma_{e1}(\Gamma_{e2})$ is the electronic relaxation constant following the arrival of pump 1(2). Note $A_1(A_2)$ and $\Delta\omega_1(\Delta\omega_2)$ are approximately proportional to the carrier density excited by pump 1(2). The oscillatory component of the composite response can be simplified as

FIG. 4. The dependence of the fitting parameters on inter-pump delay for four different data sets of varying pump fluence combinations: (*left*) (a) phonon amplitude (b) phonon decay constant (c) phonon frequency and (d) phonon phase; (*right*) (e) fast decay amplitude (f) slow decay amplitude and (g) offset. Superimposed on the phonon parameters are the results obtained from fitting the two-frequency two-oscillator model to the experimental data. Note the unusual modulations in the observed frequency and damping are reproduced quite well, particularly in the lowest fluence measurement.

$$Q_1 + Q_2 = \sqrt{A_1^2 e^{-2\Gamma_{p1}\tau} + A_2^2 + 2A_1A_2 e^{-\Gamma_{p1}\tau} \cos[\omega_1\tau + \phi(t)]} e^{-\Gamma_{p2}t} \cos\{\omega_2 t + \tan^{-1} \frac{A_1 e^{-\Gamma_{p1}\tau} \sin[\omega_1\tau + \phi(t)]}{A_2 + A_1 e^{-\Gamma_{p1}\tau} \cos[\omega_1\tau + \phi(t)]}\}. \quad (4)$$

If the phase difference is not a function of t , *i.e.* $\phi(t) = 0$, Eq. 4 would be identical to the interference

of two damped oscillators²². In this case, a single oscillator is sufficient to describe the system and one would not see a strong modulation in phonon damping. When the phase difference between the two oscillations depends not only on the delay between them but also on the elapsed time, the time-dependences of the amplitude and phase factors would cause the modulation in the observed phonon damping and frequency respectively, even though the real phonon damping and frequency are nearly constant. If we assume a linear dependence, meaning there is a small frequency difference between the two oscillators, we find that this two-oscillator model agrees well with the measured data as shown in Fig. 4. In this case, the modulations in the damping can be explained in terms of a combination of an ordinary exponential decay plus the envelope created by two beating oscillators. Since this beating occurs on a time scale comparable to the exponential decay, we see what appears as a faster or slower decay depending on the initial phase of the envelope. However, the physical reason for the frequency difference remains unclear. One possible explanation is depth inhomogeneity due to finite optical penetration depth and carrier diffusion, which would lead to different local vibrational frequencies as a function of depth into the sample. However, our simulations¹⁷ suggest that this is a small effect. Pump beam inhomogeneity can be ruled out by the fact that our results were reproducible using a conventional pump-pump-probe setup where the probe spot size was more than 10 times smaller than the pump size.

In addition to the strong modulation caused by the interference of two oscillators, there are two additional features of note in the observed phonon damping rate. First, the damping rate increases as the carrier density increases in agreement with single-pump data²³. Second, the damping rate does not correlate with the phonon amplitude in our data. This last observation indicates that anharmonic coupling that includes higher-order terms in the A_{1g} amplitude does not play an important role in the decay of the A_{1g} mode. At all fluences investigated here, the anharmonic decay is likely dominated by third-order coupling between the optical phonon and two acoustic phonons, which is linear with the A_{1g} amplitude^{19,24}.

The fluence dependence of the phonon frequency qualitatively agrees with the electronic bond softening model⁴. Furthermore, there is a slow recovery in the phonon frequency as the carriers excited by the first pump relax into the valence band and/or diffuse into the bulk of the sample. Since the time-dependent phase couples to the frequency, there is a sudden change in phonon frequency when the phonon phase changes rapidly. We do not observe clear evidence of lattice anharmonicity, *i.e.* an increase in phonon frequency at small phonon amplitudes. In our data, the phonon frequency is not modulated at a doubled frequency as shown in reference¹⁰, which may have resulted from crosstalk between the phonon frequency and chirp in the fitting process.

The DC component σ_3 in our trace indicates the lat-

tice temperature rise after electron-lattice thermalization, which usually occurs in tens of picoseconds after excitation. In the case of high fluence, we observe an anticorrelation between σ_3 and the phonon amplitude: when the A_{1g} mode is suppressed, σ_3 is higher so the final lattice temperature is lower. In order to interfere destructively with the coherent phonons created by the first pump, the second pump should arrive near one of the peaks of the transient reflectivity, where the absorption is minimum. For the peak-to-peak phonon amplitude of $\Delta R/R = 2\%$ induced by the first pump, the modulation in absorbed energy of the second pump can be estimated by $R \times 0.02/(1 - R) \approx 5\%$, which is slightly smaller than the modulation of $\sim 9\%$ observed in σ_3 .

There are two pathways which transfer the absorbed laser energy from hot carriers and coherent phonons to the lattice in the form of heat: incoherent electron-phonon coupling and anharmonic decay of coherent phonons. At high fluence, the latter process is faster than the former, and the amount of energy dissipated by coherent phonons following strong excitation can be significant enough to cause photodamage and nonthermal melting²⁵. Therefore when the coherent phonons are suppressed by the second pump pulse, the absorbed energy can only be dissipated through electron-phonon coupling, so the lattice temperature at any short time following the second pulse must be lower than it would be if the second pulse were timed to generate a large-amplitude vibrational coherence whose dissipation heated the lattice rapidly¹¹. Since our observation window is only 10 ps, this effect may appear in the value of the fitting parameter σ_3 .

The monotonic decays can result from either recovery of the equilibrium lattice position or the relaxation of hot carriers. According to DFT models, the potential minimum and its curvature are influenced by the carrier density⁴, electron temperature²⁶, and electron entropy²⁷. In all cases, the recovery of the phonon equilibrium position and phonon frequency is at the same rate as that of carrier relaxation (including electron cooling, recombination, and diffusion), which shows up as the slow decay rate σ_2 with corresponding fluence-dependent time constant 4 - 9 ps in our data. This assumption agrees with femtosecond x-ray diffraction experiments, where the recovery time of the equilibrium position is 7.6 ps at 1.1 mJ/cm²²⁸.

The origin of the fast decay σ_1 with fluence-dependent time constant 0.5 - 1 ps and the modulation we observed is still unclear. The phase of the modulation in σ_1 relative to the phonon amplitude varies with fluence¹⁷. We believe there are multiple sources of the fast decay that could couple with the phonon oscillation, including carrier diffusion and intervalley scattering. Diffusion would lead to a non-exponential decay of the surface carrier density with a fast initial drop and a slowly descending tail. According to our simulations involving diffusion, the two time constants are similar to those observed experimentally. When the A_{1g} mode is suppressed, the energy re-

mains in hot carriers and carrier diffusion is then enhanced, leading to an increase in the amplitude of the fast decay.

The fast decay may also be related to carrier relaxation at the T point²⁰ via intervalley scattering. In the low fluence regime, the electron thermalization time has been measured to be 0.6 ps²⁹ but the electron-hole recombination rate is still slow ~ 24 ps³⁰ due to the low density of states near the Fermi level. In highly excited bismuth, as bismuth nuclei move closer to the center of the unit cell, the Peierls distortion is reduced so the bandgap at the T point is smaller and the density of states drops as it approaches the Fermi level. In this case, more excited carriers are expected to reside in the T pocket and the intervalley scattering between T and L may be slower than the commonly expected femtosecond timescale. The modulation in the monotonic decays may suggest that the carrier density or distribution in the conduction band depends on the phonon location when the second pump

arrives.

IV. CONCLUSIONS

In summary, we demonstrate that phonon motion in bismuth under double excitation can be modeled by the interference of two oscillators. The lattice anharmonicity along the trigonal axis has negligible effects under most cases. We also show some control over the transient near-surface lattice temperature in the second electronic excited state based on the amplitude of the coherent phonons whose dissipation results in rapid lattice heating.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grants CHE-1111557 and 1665383 and by Office of Naval Research Grant N00014-120100530. We thank Stephen Fahy and David Reis for useful discussions.

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