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Laser-induced phonon-phonon interactions in bismuth

Eeuwe S. Zijlstra,* Larisa L. Tatarinova, and Martin E. Garcia
Theoretische Physik, Universität Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany
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We compute laser-induced interactions between coherent phonons in bismuth and demonstrate that they are key to understanding important experiments performed with intense femtosecond laser pulses. In particular, we find mixing signals and higher harmonics arising from the coupling between phonons of different and the same symmetries, respectively. We show that the phonon-phonon interaction is strongly dependent on the laser fluence and is for that reason only observable when sufficiently strong laser pulses are used. Our results offer a unified description of the different experimental observations performed so far on bismuth.

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Intense femtosecond laser pulses may induce nonequilibrium states, leading to sudden and dramatic changes in the potential energy surfaces of different solids.[1] This can be exploited to excite and manipulate coherent lattice vibrations, as has been recently shown by several experiments[2–5] and simulations.[6] In recent years, a variety of experiments on the laser excitation of coherent phonons has been performed on bismuth,[7–10] which is a particularly interesting solid due to a Peierls distortion in its ground state structure. However, from recent experimental studies, reaching unprecedented time and frequency resolutions, a number of fundamental aspects still remains unexplained, like the detection of higher harmonics[8] and the appearance of modes that are forbidden by symmetry in the isotropic reflectivity.[7]

In bismuth, coherent phonons of two different symmetries are excited by lasers,[4] as has been verified in separate experiments: On the one hand, A_{1g} phonons, which correspond to the motion of the atoms in the direction of the Peierls distortion, have been studied through changes in the isotropic reflectivity[7,8] and through changes in geometrical structure factors.[9] E_g phonons, corresponding to an atomic motion in the perpendicular plane, on the other hand, have been observed using electro-optical techniques.[11] So far, however, coherent A_{1g} and E_g phonons have not been described in a unified way and interactions between these two phonon modes, which become important at high amplitudes, have not been considered.

In this Rapid Communication we show that intense ultrashort laser pulses do not only induce coherent phonons in bismuth but also interactions between them. This conclusion is based on dynamical simulations for the E_g and A_{1g} degrees of freedom using potential energy surfaces that we obtained from all-electron density functional theory (DFT) calculations. By treating the A_{1g} and E_g phonons on a common footing we provide a unified picture explaining all experiments that have been performed to date on laser-excited coherent phonons in bismuth. By invoking laser-induced phonon-phonon interactions we explain the following experiments, which so far have not been well understood. (i) Higher harmonics of the A_{1g} phonon frequency have been detected.[8] (ii) In isotropic reflectivity measurements apart from the softened A_{1g} phonon mode a signal at a lower frequency that can be attributed to the E_g phonons has been found.[7] (iii) There is also a peak at a higher frequency that has not been accounted for.[12]

The atomic structure of Bi can be derived from a simple cubic atomic packing in two steps. First a simple cubic lattice is deformed by elongating it along one of the body diagonals (indicated by a thin line in Fig. 1). A Peierls instability then causes the atoms to be displaced along the same diagonal, in opposite directions (Fig. 1). The magnitude of the displacements is determined by the interactions between the Bi nuclei and the electrons. When the electrons are heated with a laser, the equilibrium positions of the atoms change. If the duration of the laser pulse is short in comparison with the time scale of the atomic motion, the ions are lifted at their original equilibrium positions to the potential energy surface that is created by the hot electrons, from where they start to swing about their new equilibrium positions.[2] This motion of the atoms corresponds to the coherent displacive excitation of the A_{1g} phonons (Fig. 1). Coherent E_g phonons, which correspond to the motion of the atoms in the plane perpendicular to the elongated body diagonal, are excited impulsively through Raman scattering.[4]

For our ground state DFT calculations we used the experimental unit cell parameters.[13] In Ref. 14 it has been shown that DFT optimized lattice parameters are not expected to significantly change the results for laser-excited coherent op-

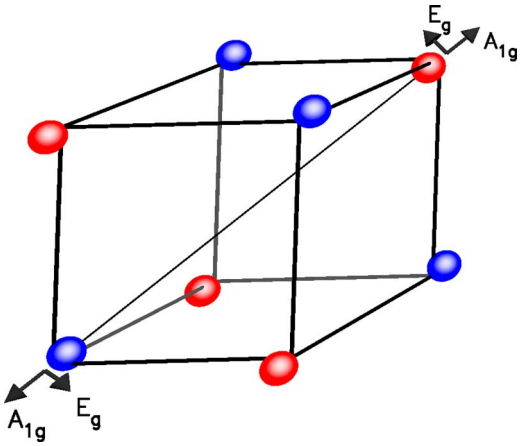

FIG. 1. (Color online) Structure of Bi (see text). In the A_{1g} phonon mode the atoms move in the direction of the thin line as indicated for two atoms (long arrows). In the E_g phonon modes the atoms move in the perpendicular plane (e.g., in the directions of the short arrows).

TABLE I. Coefficients for the potential energy surfaces of Eq. (1) as a function of the electronic entropy S_e. In Eq. (1) E_{tot} is given in mRy / atom, x and y are given in units of the lattice parameter a, and z is given in units of c. The electronic temperature T_e and the number of electron-hole pairs $N_{e\text{-}h}$ (expressed in percent of the valence electrons), which are not constants of motion, are given for $z=0.234$.

S_e (k_B/atom)	T_e (mRy)	$N_{e\text{-}h}$ (%)	a_0	a_1 (10^4)	a_2 (10^8)	a_3 (10^{11})	a_4 (10^{14})	b_0 (10^3)	b_1 (10^7)	b_2 (10^{10})
0.164	12.7	0.50	−12.087	−3.0663	1.2609	−2.1728	1.7787	−3.35	4.202	−7.48
0.260	16.2	0.81	−11.428	−2.4474	1.0267	−1.6487	1.3035	−2.52	3.360	−5.30
0.300	17.6	0.95	−11.039	−2.2087	0.9417	−1.4619	1.1342	−2.21	3.070	−4.58
0.431	22	1.42	−9.346	−1.5328	0.7272	−1.0200	0.7452	−1.34	2.380	−2.96

tical phonons, which we study in this work. The Bi atoms occupied the 6c sites $(0,0,z)$, where z gives the position of the atoms along the above-mentioned diagonal. We performed DFT calculations varying z around the equilibrium value $z=0.234$.[15] Based on the total energies we could perform a simulation of the coherent A_{1g} phonons. The degrees of freedom corresponding to the E_g phonons (x and y) were taken into account by simultaneously varying x and z.[16] The potential energy surface, on which the ions moved, was fitted to the function

$$E_{\mathrm{tot}} = \sum_{p=0}^{4} a_p (z-0.25)^{2p} + (x^2+y^2) \sum_{p=0}^{2} b_p (z-0.25)^{2p}, \quad (1)$$

where the last term describes a coupling between the motion in the z and the x (y) directions. The fact that it is to lowest order proportional to (x^2+y^2) and does not have terms linear in x and y can be easily understood from the symmetry of the crystal structure, since the coupling cannot depend on the sign of the displacement (see Fig. 1). Other important details of our DFT calculations were as follows. We used the all-electron full-potential linearized augmented plane wave (LAPW) computer program WIEN2K.[17] LAPWs with energies up to 12.0 Ry were included in the basis. Inside the atomic spheres (with radii of 1.376 Å) additional 5d, 6s, 6p, and 6d local orbitals were used. Spin-orbit coupling was treated in a second variational procedure, where the scalar relativistic eigenstates up to 3.0 Ry and local $6p_{1/2}$ orbitals were used as a basis for the relativistic calculation. The entire Brillouin zone was sampled with 512 **k** points using temperature smearing ($T_e=1$ mRy).

At elevated temperatures we assumed that there was no exchange of heat between the electrons and the ions. As a consequence the entropy of the electrons was a constant of motion.[18] We further assumed that the electrons were perfectly thermalized at all times due to electron-electron interactions.[19] Therefore the occupation numbers of the Kohn-Sham states were always given by a Fermi-Dirac distribution. Recently, another approach has been proposed,[10,14,20] where the occupation numbers for the electrons and holes of laser-excited Te[14,20] and Bi[10] are modeled with two temperature distributions using different chemical potentials for the electrons and the holes while keeping the number of electron-hole pairs constant. Although this so-called two-chemical-potential model might work well for semiconductors, we do not believe that it is appropriate for Bi at high laser fluences as we discuss below.

To compare the predictions of the two-chemical-potential model and the model where the constant entropy of the electrons was the only constraint we performed additional calculations assuming two chemical potentials. In agreement with Ref. 10 we chose the electron and hole temperatures $T_e=T_h=0.5$ eV at $z=0.234$. No heat was assumed to be exchanged between the electrons or the holes and the ions. Therefore the entropy of the electrons and holes were constants of motion. In this respect we did not follow the method of Refs. 10, 14, and 20, where the temperatures of the electrons and the holes have been kept constant, while the atoms moved on the total energy surface, because it yields incorrect forces.[21]

The potential energy surface $E_{\mathrm{tot}}(T_e)$ on which the ions moved at elevated electronic temperatures was calculated from

$$E_{\mathrm{tot}}(T_e) = E_{\mathrm{tot}}(\mathrm{gs}) + \Delta E_{\mathrm{band}}, \quad (2)$$

where $E_{\mathrm{tot}}(\mathrm{gs})$ was the self-consistent total energy of the electronic ground state and $\Delta E_{\mathrm{band}}=E_{\mathrm{band}}(T_e)-E_{\mathrm{band}}(\mathrm{gs})$. This approach is based on the interpretation of the Kohn-Sham energies as single-electron excitation energies. In standard temperature-dependent DFT the electronic occupation numbers are incorporated in the self-consistent cycle to take into account possible screening effects. We also performed such standard temperature-dependent DFT calculations and found that the differences between the predictions of both approaches were very small. For this reason and also because it is not clear that the self-consistent approach always leads to better results we used the computationally less time-consuming non-self-consistent treatment of Eq. (2). Our results for different laser-induced initial electronic temperatures are summarized in Table I.

In the electronic ground state the total energy E_{tot} was minimized for $z=0.2346$. At this parameter the A_{1g} and E_g phonon frequencies were 2.89 and 1.94 THz, respectively, in reasonable agreement with experiment[22] and with earlier calculations.[23] The differences with the experimental results are probably due to the local density approximation,[24] which we used for the exchange and correlation energy. The differences with the earlier calculations are probably due to the Bi pseudopotential used in those calculations. The present all-electron calculations do not rely on a pseudopotential and should be more accurate.

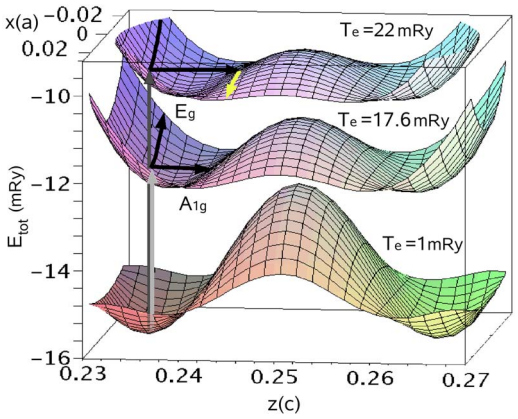

FIG. 2. (Color online) Potential energy surfaces for the ground state (T_e=1 mRy) and for excited electronic states (T_e=17.6 and 22 mRy at z=0.234). Vertical arrows show transitions of the atoms from the ground state to an excited energy surface. The A_{1g} and E_g phonon modes are indicated. On the surface labeled T_e=22 mRy the curvature in the x direction becomes negative when the atoms are at their maximal displacement in the z direction. This negative curvature is indicated by a light arrow.

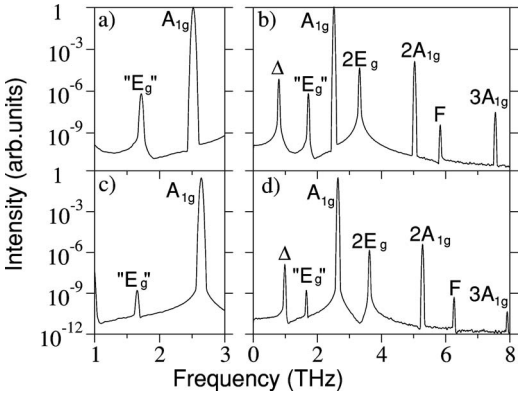

FIG. 3. Fourier transforms (intensities) of the z coordinate of the atoms for two different simulations: (a), (b) T_e=16.2 and (c), (d) T_e=12.7 mRy at z=0.234. All curves have been convoluted with a Gaussian with a full width at half maximum of 0.03 THz. The left panels (a) and (c) show that the height of the peak labeled "E_g" depends very sensitively on the laser fluence, which was twice lower in (c) than in (a). Experimentally this has been shown in Ref. 7.

In the excited electronic states (Table I) the potential energy surfaces are flatter than the ground state potential energy surface (Fig. 2). As a consequence the phonon frequencies are lower. In addition anharmonicity may further lower the phonon frequencies.[7,25] After the initial softening of the A_{1g} phonons, the frequency returns to its original value within roughly 10 ps.[7] We discuss the origin of this frequency hardening by comparing our results and the experimental results of Ref. 7, where the A_{1g} phonon frequency has been resolved in time. For the electronic entropy S_e =0.300 k_B/atom (Table I) our calculated A_{1g} phonon frequency was 2.45 THz, the initial A_{1g} frequency obtained in Ref. 7. After 0.3 ps the A_{1g} frequency in Ref. 7 increased to 2.52 THz. Our results indicated that at most 0.03 THz of this increase can be explained by the anharmonicity of the potential energy surface (the harmonic frequency was 2.48 THz), in agreement with experiments using two time-delayed pump laser pulses[10] that have shown that the frequency of the A_{1g} phonon mode averaged over five periods is the same within 1% independent of the amplitude of the oscillations for frequencies as low as 2.65 THz. Instead a decrease of the electronic entropy to S_e=0.260 k_B/atom yielding an A_{1g} frequency of 2.52 THz is probably responsible for the frequency increase observed in Ref. 7. The accompanying decrease in the number of electron-hole pairs by 15% (calculated at z=0.234) corresponds to a decay time of 1.8 ps, which agrees well with the experimentally determined electronic background decay time of 1.78±0.08 ps, which is independent of the laser fluence.[26] The loss of entropy of the electrons near the surface is most likely due to diffusion of hot electrons away from the surface region (the penetration depth of the laser $d \approx 17$ nm) and may also be partly due to the exchange of heat of the electrons with the ions via electron-phonon coupling, two processes that were not explicitly taken into account in our calculations.

We now consider the coupling between the A_{1g} and the E_g phonons. Figures 3(a) and 3(b) show the intensity of the Fourier transform of the z coordinate of the atoms. Higher harmonics of the main A_{1g} peak at 2.52 THz, which have also been observed experimentally,[8] and which are a consequence of the anharmonicity of the potential, are indicated. For the initial velocity of the atoms in the x direction (coherent E_g phonons) we chose a value that gave a peak-to-peak amplitude $\Delta x = 0.4\Delta z$, in agreement with Ref. 27. In Fig. 3(b) it is clear from the peaks that are not higher harmonics of the main frequency that there is a considerable coupling between the A_{1g} and E_g phonons. In Eq. (1) the A_{1g} phonon mode couples to x^2+y^2, a signal with double the E_g frequency, $2\nu(E_g)$. Accordingly an analysis of the x coordinate of the atoms showed that the frequency of the highest peak induced by the coupling between the A_{1g} and E_g phonons, labeled $2E_g$ in Fig. 3(b), (3.32 THz) equaled $2\nu(E_g)$. Experimentally this peak has been observed at 3.44 THz.[12] So in our calculations $\nu(E_g)$ was slightly lower than in the experiment,[12] which is consistent with our ground state calculation. The frequency of the peak labeled "E_g" in Fig. 3(b) (1.72 THz) is given by $2\nu(A_{1g}) - 2\nu(E_g)$. Experimentally this peak has been observed at 1.61 THz.[7] Our value was slightly higher than in the experiment[7] because the calculated $\nu(E_g)$ was slightly lower. Note that in Ref. 7 this peak has been identified with the E_g mode. However, since there is no coupling term linear in x (y), and since the E_g mode produces modulations of the A_{1g} oscillations, it is clear that no peak of the power spectrum can have the frequency $\nu(E_g)$, whereas the difference $2\nu(A_{1g}) - 2\nu(E_g)$ should be present. The fact that the "E_g" peak has an intensity of only $I(\text{"}E_g\text{"}) = 7 \times 10^{-7} I(A_{1g})$ and that it has nevertheless been observed experimentally[7] indicates that the laser-induced amplitude of the E_g mode is probably larger than $\Delta x = 0.4\Delta z$, which we used in our simulation. According to Ref. 27 the relative Raman cross sections of the A_{1g} and E_g modes are indeed temperature dependent. The sensitivity of the results to the initial conditions is further underlined by a calculation with $\Delta x = 1.2\Delta z$, for which we found $I(\text{"}E_g\text{"}) = 3 \times 10^{-4} I(A_{1g})$. Finally, we note

that the peak labeled Δ in Fig. 3(b) $[2\nu(E_g)-\nu(A_{1g})]$ is experimentally hard to observe because of broadened spectral structures near zero frequency.[12] Similarly the peak labeled *F* in Fig. 3(b) $[2\nu(E_g)+\nu(A_{1g})]$ probably has too low an intensity to be observed.

Figures 3(c) and 3(d) were calculated for the case where the energy absorbed from the laser was twice as small as in Figs. 3(a) and 3(b): We found that the intensity of the peak "E_g" became orders of magnitude lower. This showed that the laser-induced phonon-phonon interaction depended strongly on the laser fluence. Therefore a strong laser pulse is needed to observe the $A_{1g}-E_g$ phonon coupling, which has also been found experimentally in Ref. 7.

Another interesting result that we found is that the coupling between the A_{1g} and E_g modes became very strong for $S_e \gtrsim 0.431 k_B$/atom: The curvature of the potential energy surface in the *x* direction became negative every time *z* reached its maximum value (Fig. 2). We found that in this case the amplitude of the E_g mode increased exponentially even when the initial velocity in the *x* direction was very small.

We now discuss the limitations of the two-chemical potential model proposed in Ref. 14. According to Ref. 28 the electron-hole recombination time in Bi at 300 K is about 1 ps. In a highly excited electronic state this time is expected to be considerably shorter. So within less than four phonon periods the electrons and the holes obtain a common chemical potential. To check the validity of the two-chemical-potential model we applied it and found that the chemical potential of the holes was greater than the chemical potential of the electrons, which means that upon reaching a common chemical potential the number of electron-hole pairs would increase, which would then give rise to a substantial further lowering of the phonon frequencies (we estimated that the ions would even go over the barrier at $z=0.25$), in contradiction with experiment.[7] Therefore we believe that the two-chemical potential model[10] does not provide a realistic description of the electron dynamics in Bi. We can, however, not exclude that this model might be appropriate for semiconductors or for Bi at lower laser fluences.

Summarizing, we have shown that the potential energy surfaces of the excited states created by high intensity femtosecond laser pulses cannot be described by a series of independent, harmonic oscillators. Instead, the phonon modes become anharmonic and the coupling between them cannot be ignored. We found that these laser-induced phonon-phonon interactions are responsible for the appearance of higher harmonics and mixing signals that have been measured, but were so far not well-understood.[7,8,12] More generally, our results were in good agreement with all experiments performed to date.[7–12] Finally we argued that a much-used model involving two Fermi-Dirac distributions for the electrons and the holes[10,14,20] is unphysical for Bi at high fluences.

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*Electronic address: zijlstra@physik.uni-kassel.de

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