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Ultrafast photoinduced structure phase transition in antimony single crystals

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Picosecond Raman scattering is used to study the photoinduced ultrafast dynamics in Peierls distorted antimony. We find evidence for an ultrafast nonthermal reversible structural phase transition. Most surprisingly, we find evidence that this transition evolves toward a lower symmetry in contrast to the commonly accepted rhombohedral-to-simple cubic transition path. Our study demonstrates the feasibility of ultrafast Raman scattering symmetry analysis of photoinduced nonthermal transient phases.

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Controlling the state of a material through light irradiation, and thereby obtaining transient highly-off-equilibrium phases, is one of the intriguing achievements in condensed-matter science of the last decade.[1–4] Progress in this field has been boosted by the easy availability of extremely short light pulses (10^{-14} s), kindling the hope of controlling matter on ultrafast time scales, i.e., on time scales faster than the characteristic thermodynamical time scale which limit the speed of current phase change media based devices. The main emerging limitation in bidirectional ultrafast optical switching is that by and large the photoinduced phase transitions reported to date are low-to-high symmetry transitions. Rare are the examples of photoinduced high-to-low symmetry transitions necessary to complete the ultrafast bidirectional switching cycle and controversial is the possibility of photoinducing a high-to-low symmetry phase transition on ultrafast time scales.[5,6] While the low-to-high symmetry phase transition can occur through direct coupling of the light field (carrying little momentum) to crystal excitations, the reduction in symmetry can only arise due to a cooperative effect leading to self-organized long-range order which is usually limited to occur on “thermodynamic” time scales.

Group V semimetals such as bismuth and antimony have served as a playground for studying interactions between ultrafast light pulses and absorbing matter.[7–10] The strong coupling between the structural and electronic degrees of freedom in these materials allowed for the first pioneering studies in the late 80s and early 90s on “coherent phonon” generation in absorbing materials, visualizing the real time behavior of optical phonons.[11–13] More recently the structural and electronic dynamics following laser irradiation in Bi and Sb single crystals have been studied in great detail and the possibility of inducing a “nonthermal” phase transition to a simple cubic phase has been discussed on the base of *ab initio* calculations.[14–16] The structure of the A7 compounds [sketched in Fig. 1(a)] may be described as a distorted simple cubic structure, where the (111) planes of atoms have an alternating displacement along the [111] direction. This structural peculiarity of the semimetals Bi, Sb, and As has been widely discussed in the past[17–19] and originates from a strong electron phonon coupling. In one dimension, this type of distortion is the well known Peierls distortion.[20,21]

The physics behind the expected photoinduced effects in the A7 semimetals can be sketched in a simple way. Photoexcitation of valence-band electrons increases the electron density in the conduction band thereby reducing the energy gain of the Peierls distortion. Eventually this renders the Peierls distortion unstable and a phase transition should occur to the undistorted phase on a time scale faster than the time required for electron-phonon thermalization. The *ab initio* calculations indicated that the cubic phase should be reached for a critical excitation density of 2.7%.[14] Various experimental studies have tried to reach this excitation limit in the A7 semimetals making use of a variety of techniques including time-resolved reflectivity,[22] x-ray diffraction,[16,23] and UV absorption experiments.[24] In spite of the experimental efforts devoted, no evidence of an optically induced reversible phase transition has been reported so far.

The current work presents an ultrafast time-resolved Raman spectroscopy study of Sb single crystals.[30] This technique is sensitive to transient changes in the crystal structure through transient changes in the spontaneous vibrational Raman response. In addition, the ratio between Stokes and anti-Stokes intensities allows to distinguish the dynamics induced by lattice heating from nonthermal effects arising from electronic screening of the crystal potential. The experiments reveal two distinct dynamics: a fast nonthermal response occurring in the first few picoseconds after irradiation and a slower thermal one which lasts for more than 100 ps. The short time response evidences the existence of an induced transient state even though the nature of this state deviates from the expected simple cubic phase.

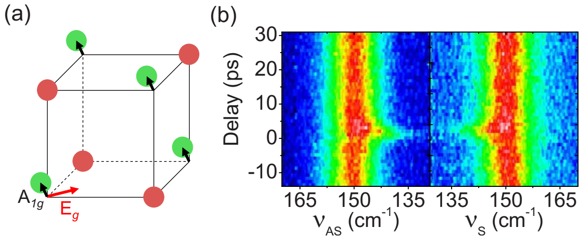

FIG. 1. (Color online) (a) Equilibrium structure of the A7 semimetals. The A_{1g} vibrational mode corresponds to a modulation of the distance between the (111) planes, while the E_g mode corresponds to a sliding of adjacent (111) planes. (b) False color plot of the time-resolved Stokes (right) and anti-Stokes (left) Raman data for an excitation density of 4.6 mJ/cm^2.

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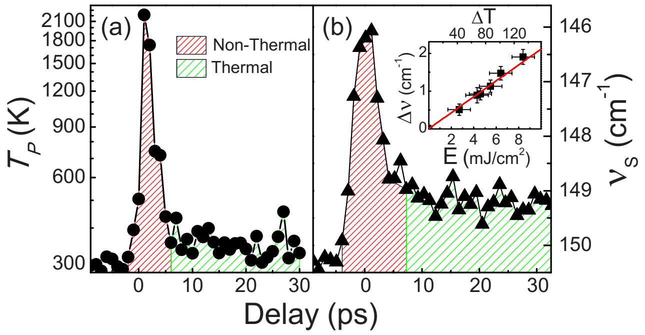

FIG. 2. (Color online) Time evolution of (a) the A_{1g} phonon temperature T_P and of (b) the central frequency of the Stokes line after excitation with 4.6 mJ/cm^2. The inset in (b) shows the frequency shift of the A_{1g} phonon at 20 ps delay versus the pump excitation density and corresponding calculated temperature change (symbols). The drawn line shows the temperature dependence of the frequency shift obtained from continuous wave Raman experiments.

The experiments were performed using a 80 MHz picosecond Ti:sapphire laser (MIRA 900, wavelength 800 nm, pulse duration 1.7 ps) as excitation laser, which was coupled using a custom designed pump-probe scheme to the microscope of a standard charge coupled device equipped Raman spectrometer (T64000, Jobin Yvon).[25] All experiments have been performed at ambient conditions in a controlled argon environment. Figure 1(b) shows the time evolution of the A_{1g} mode in antimony after excitation with a moderately low pump power density (4.6 mJ/cm^2). The right and left panels display a false color plot of the Stokes and anti-Stokes response, respectively. In the first few picoseconds after excitation, the A_{1g} mode shows a rapid and appreciable softening toward the low energy side with a subsequent relaxation, in roughly 10 ps, to a transient spectrum which is close to the equilibrium one. This transient state slowly relaxes to the equilibrium situation with a decay time exceeding 100 ps. The ratio of the integrated intensity of the Stokes and anti-Stokes spectra allows extraction of the nonequilibrium phonon "temperature" as a function of time. The evolution of this temperature after pump excitation (4.6 mJ/cm^2) is depicted in Fig. 2(a). In the first 3 ps the phonon temperature rises to more than 2000 K. Clearly this does not correspond to a thermodynamic temperature rise but merely reflects the nonequilibrium phonon occupation which is boosting the anti-Stokes response relative to the Stokes response. On the same time scale, however, also the frequency of the A_{1g} mode softens considerably [see Fig. 2(b)] to values which are not achievable under equilibrium conditions (at atmospheric pressure[26]). This indicates that not only population effects, but also electronic screening occurs on this time scale. We will return to discuss the fast response later on after having discussed the nature of the spectral changes at large positive times ($t > 10$ ps).

Equilibrium between the electronic and the lattice temperature is reached in about 10 ps after pump irradiation. Based on the equilibrium thermodynamical and optical properties of Sb, one can estimate the expected temperature rise resulting from the photoexcitation. As an example, based on the reflectivity, optical penetration depth, and heat capacity of Sb, one expects that excitation with a density of 4.6 mJ/cm^{-2} results in a temperature rise of approximately 80 K. This is indeed what is observed experimentally [see Fig. 2(a)]. The temperature rise estimated from the intensity of the anti-Stokes signals is confirmed by the frequency shift of the A_{1g} phonon to 149 cm^{-1} [Fig. 2(b)], which is the expected value for Sb at 370 K.[27] The residual frequency shift observed at times larger than 10 ps confirms the completed thermalization between the electronic and lattice subsystems. This is further illustrated in the inset of Fig. 2(b), which compares the frequency of the A_{1g} mode as a function of the measured phonon temperature at 20 ps after excitation (symbols) with the result of continuous wave Raman measurements as a function of the thermodynamic temperature[27] (drawn line). The good agreement of the experimental and estimated temperature at late times indicates that diffusive heat transport by photoexcited electrons is less efficient than energy relaxation to the lattice. Nearly all the energy dumped by the optical pulse and adsorbed by the electronic subsystem results in local lattice heating within 10 ps. Vibrational and electronic heat diffusion only play a significant role at later times when the system slowly relaxes back to the initial state ($t > 100$ ps).

Now we turn back to the ultrafast response. Two features clearly evidence the nonthermal nature of the processes occurring at early times following laser irradiation. First, the calculated phonon temperature in the first 10 ps reaches values up to 2200 K, well above the equilibrium melting temperature of antimony (903 K). Second, the frequency of the A_{1g} mode in the first 10 ps reaches values lower than those measured under equilibrium conditions at any temperature up to the melting point. Such low frequencies have only been observed in pressure-dependent experiments in the GPa range.[28] The observed nonthermal phonon softening is comparable to the one measured in the time domain with similar electronic excitation densities clearly demonstrating that the electronic screening of the crystal potential induces a large phonon softening and that anharmonicity only plays a minor role, if any. One of the most striking observations it that the line shape for the first few picoseconds after excitation is substantially different for low and high excitation densities. This is illustrated in Fig. 3, where panels (a) and (b) show the Raman response in the region of the A_{1g} mode at different times for low (2.7 mJ/cm^2) and high (8.4 mJ/cm^2) excitation densities, respectively. Both before arrival of the pump pulse as well as at late times the phonon response shows a standard Lorentzian shape (L1) for both excitation densities. In contrast, the early time responses differ drastically. For moderately low power density (<5 mJ/cm^2) the A_{1g} phonon shifts to lower frequency, keeping a Lorentzian shape response with approximately the same linewidth as measured before pumping, indicating that the A7 structure is retained. This is no longer true for power densities exceeding ~ 5 mJ/cm^2. In this case the early time Raman spectrum shows, apart from the normal response (L1), the appearance of a new shoulder (L2) at the low energy side. This strongly suggests that at high excitations density the symmetry of antimony has changed substantially in the first few picoseconds, i.e., that an optical phase transition has occurred. Fur-

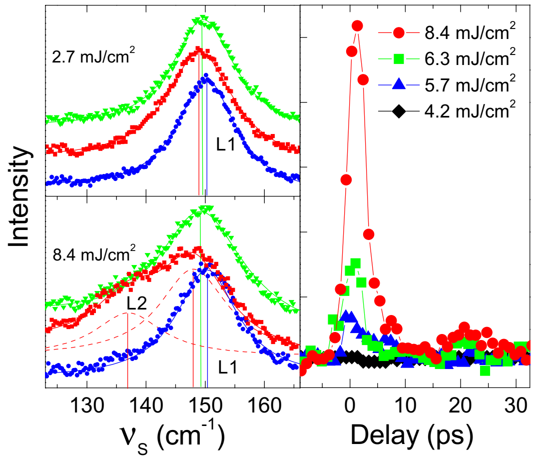

FIG. 3. (Color online) Raman response for the unperturbed system ($t=-10$ ps, blue dots) for the ultrafast nonthermal response ($t=1$ ps, red squares) and for the thermal response ($t=20$ ps, green triangles) for pump excitation densities 2.7 mJ/cm^2 (a) and 8.4 mJ/cm^2 (b). The dashed lines in (b) show the fitted Lorentzians to the spectrum at $t=1$ ps. The right panel (c) shows the time evolution of the intensity of the new vibrational mode (L2) for various excitation densities.

ther strong evidence for this comes from the threshold behavior observed in the activation of the L2 mode as demonstrated in Fig. 4(a). The mode is only observed for excitation densities exceeding 5 mJ/cm^2 and shows a linear increase in the intensity upon further increasing the excitation density.

A two-component fit of the high excitation density spectra reveals that the additional phonon mode, unlike the L1 mode, has a time-independent frequency. Moreover, the frequency of the new mode is $\simeq 10\%$ lower than the frequency of the equilibrium A_{1g} mode and $\simeq 20\%$ higher than the E_g mode which could be activated by optically induced disorder. These observations demonstrate that this new mode is indeed not originating from the A7 structure. Finally we note that the optically induced phase has a relatively short lifetime (~ 5 ps) as shown by the time dependence of the intensity plotted in Fig. 3(c).

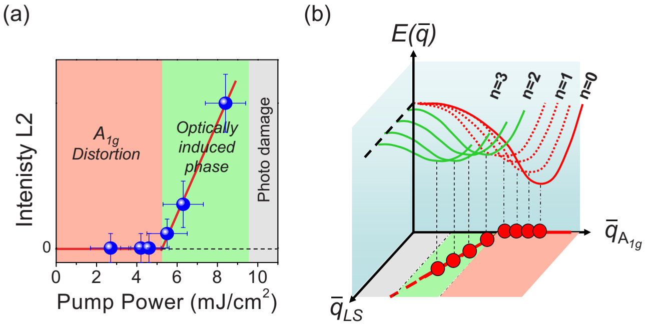

FIG. 4. (Color online) (a) Maximum intensity of the new vibrational mode (L2) of the induced phase as a function of pump power density. (b) Cartoon of the induced nonlinear dynamics in the A7 semimetals. The curves represent cuts of the free energy for a distortion along the A_{1g} direction for various charge excitation densities n. For low density excitation the minimum of the free energy stays on the fully symmetric (A_{1g}) direction thereby preserving the A7 symmetry. Excitation densities exceeding 2%(~ 5 mJ/cm^2) lead to a symmetry breaking due to displacement along a low symmetry direction $\bar{q}_{\mathrm{LS}}$.

The question now arises of what the symmetry of the new optically induced phase is. It is clear that the long expected phase transition to the high symmetry cubic phase can be excluded. For the simple cubic symmetry one expects no optical phonon mode at all, in striking contrast with the presence of the observed additional mode. Moreover, one would expect a complete softening of the A_{1g} mode which is clearly not observed. In addition, no anticorrelation between the intensities of the L1 and L2 modes has been observed indicating that the Raman spectrum of the new phase contains both L1 and L2. Therefore, we conclude that this phase has a lower symmetry than the A7 structure. Given the inhomogeneous excitation used we cannot exclude, however, that a small fraction of the L1 mode still originates from the normal phase. Another possibility would be that the new phase corresponds to one of the phases observed at high pressures (>8 GPa).[28] However, in that case one would expect a new mode on the high energy side of L1, which is not the case.

One intriguing possibility for the new phase is that the structural change is not due to a softening of the A_{1g} mode, but rather due to a E_g distortion, i.e., due to an alternating displacement of the (111) planes along a direction perpendicular to the [111] direction [indicated in Fig. 1(a)]. Such a distortion would most likely lead to a monoclinic $C2/m$ structure, with indeed an activation of additional modes in the Raman spectrum.[31]

Figure 4(b) summarizes the mechanism suggested for the optically induced phase transition in the A7 semimetals in cartoonlike fashion. The excitation of electrons into the conduction bands reduces the energy gain of the Peierls distortion forcing the ions to move toward the cubic undistorted symmetry. As the excitation density is increased the alternating distortion of the (111) planes along the A_{1g} direction reduces while retaining the overall rhombohedral symmetry. For excitation densities exceeding ~ 5 mJ/cm^2 an instability (possibly of E_g nature) sets in which reduces the A7 symmetry without ever reaching the high symmetry cubic phase. We believe that in our configuration we can explore this region of the phase diagram thanks to the fact that our measurements do not require the nonadiabatic coherent excitation of the fully symmetric A_{1g} mode for detection. In conclusion we demonstrated the feasibility of time-resolved Raman studies to unravel the interplay between electronic and structural degrees of freedom. Insights into the thermalization processes between electrons and ions have been obtained from the measured transient Raman spectra, showing the thermal nature of the crystal response for times larger than 10 ps after the pump excitation, and demonstrating that electronic energy diffusion plays a minor rule in the transient dynamics for the A7 semimetals. In the nonthermal region ($t<10$ ps) we demonstrate that the electronic screening of the crystal potential can induce a large phonon softening ruling out that anharmonicity plays an important role. Maybe the most important result of the present work is the observation of an ultrafast optically induced phase transition toward a nonthermal low symmetry phase for excitations exceeding ~ 2 electrons per 100 ions.

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[30] Similar experiments have been performed in bismuth with essentially the same results.

[31] The dispersion relations of the E_g modes (Ref. 29) show that a doubling of the unit cell would give an additional zone center mode at a frequency close to the observed one.