Ultrafast photoinduced structure phase transition in antimony single crystals

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(Received 12 October 2009; published 30 October 2009)

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.

DOI: 10.1103/PhysRevB.80.161207 PACS number(s): 78.47.jc, 78.30.--j

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 limits 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 past17–19 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,16,23 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_{1u} 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/cm².](image-url)
the reflectivity, optical penetration depth, and heat capacity of Sb, one expects that excitation with a density of 4.6 mJ/cm² 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. 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 (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. 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 is 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/cm²) and high (8.4 mJ/cm²) 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/cm²) 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/cm². 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. Further
A small fraction of the L1 mode still originates from the nonther-
mal low symmetry phase for excitations exceeding 8.4 mJ/cm². We
expect a complete softening of the A1g mode, but rather due to a
C2/m distortion, i.e., due to an alternating distortion of the (111)
planes along a direction perpendicular to the [111] direction [in-
dicated in Fig. 1(a)]. Such a distortion would most likely lead to a
monoclinic 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 con-
duction bands reduces the energy gain of the Peierls distor-
tion forcing the ions to move toward the cubic undistorted
symmetry. As the excitation density is increased the alter-
ning distortion of the (111) planes along the A1g direction reduces
while retaining the overall rhombohedral symmetry. For excitation
densities exceeding ~5 mJ/cm² an instability (possibly of Eg nature) sets in which reduces the A7 symme-
try 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 measure-
ments do not require the nonadiabatic coherent excitation of
the fully symmetric A1g mode for detection. In conclusion we
demonstrated the feasibility of time-resolved Raman studies to
unravel the interplay between electronic and structural de-
grees of freedom. Insights into the thermalization processes
between electrons and ions have been obtained from the
measured transient Raman spectra, showing the thermal na-
ture of the crystal response for times larger than 10 ps after
the pump excitation, and demonstrating that electronic en-
ergy 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 im-
portant result of the present work is the observation of an
ultrafast optically induced phase transition toward a nonther-
mal low symmetry phase for excitations exceeding ~2 elec-
trons per 100 ions.
We sincerely thank Ben Hesp, Arjen F. Kamp, and Foppe de Haan for their help in executing the experiments and analyzing the data. We also sincerely thank A. Cavalleri and M. Mostovoy for fruitful discussions and are grateful to C. Giannetti, P. Colombi, and M. Zaffalon for the critical reading of the paper. This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM),” which is financially supported by the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).”

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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.