Probing ultrafast symmetry breaking in photo-stimulated matter

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Picosecond Raman scattering is used to study the photo-induced ultrafast dynamics in Peierls distorted Antimony. We find evidence for an ultrafast non-thermal 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 photo-induced non-thermal transient phases.

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 2 3 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 timescales faster than the characteristic thermodynamical timescale 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 photo-induced phase transitions reported to date are low to high symmetry transitions. Rare are the examples of photo-induced high to low symmetry transitions necessary to complete the ultrafast bidirectional switching cycle and controversial the possibility of photo-inducing a high to low symmetry phase transition on ultrafast timescales 4 5 , while the low-to-high symmetry phase transition can occur through direct coupling of the the light field (carrying little momentum) to crystal excitations, the reduction of the symmetry can only arise due to a cooperative effect leading to self-organized long-range order which is usually limited to occur on 'thermodynamic' timescales. In contrast to this, our findings from ultrafast experiments on the A7 metals demonstrate the possibility of inducing a reversible photo-induced symmetry lowering on timescales surpassing the time needed to reach thermodynamical equilibrium.

The group V semi-metals like Bismuth and Antimony have served as a playground for studying interactions between ultrafast light pulses and absorbing matter. 6 7 8 9 The strong coupling between the structural and electronic degrees of freedom in these materials allowed for the first pioneering studies in the late-eighties, early-nineties on "coherent phonon" generation in absorbing materials, visualizing the real time behavior of optical phonons. 10 11 12 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 "non-thermal" phase transition to a simple cubic phase has been discussed on the base of ab-initio calculations. 13 14 15 16 The structure of the A7 compounds (sketched in Fig.1) 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 semi metals Bi, Sb, and As has been widely discussed in the past 17 18 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 photo-induced effects in A7 metals can be sketched in a simple way. The photo-excitation of valence band electrons increases the electron density in the conduction band and, as a consequence, it reduces 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 mentioned earlier indicated that the cubic phase should be reached for a critical excitation density of 2.7 electrons per hundred ions. 13 16 Various experimental studies have tried to reach this excitation limit and to detect an optically induced phase transition in Bismuth and Antimony single crystals making use of a variety of techniques, including time-resolved reflectivity, 22 x-ray diffraction, 15 24 and UV absorption experiments. 24 In spite of the experimental efforts devoted, no evidence of an optically induced reversible phase transition in the A7 semimetals has been reported so far under any of the explored excitation conditions.

The current work presents results of an ultrafast time resolved Raman spectroscopy study of Antimony single crystals 28 . This technique is sensitive to transient changes in the crystal structure through transient changes in the spontaneous vibrational Raman response. In addition to this, a comparison between the Stokes and anti-Stokes scattering intensity allows to distinguish the
dynamics induced by lattice heating effects from the non-thermal ones arising from the electronic screening of the crystal potential. The experiments reveal two distinct dynamics: A fast non-thermal response occurring in the first few picoseconds after irradiation, and a slower thermal one which lasts for more than 100ps. 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.

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). All experiments have been performed at ambient conditions in a controlled Argon environment.

![FIG. 1: (a) Equilibrium structure of the A7 semimetals (space group R3m). The A1g 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 (left) and anti-Stokes (right) Raman data for excitation density of 4.6mJ/cm². (c) False color plot of the pump-probe Raman data for various pump intensities. (d) Optically induced changes in the Raman spectra obtained by the subtraction of the negative time response from the data in (c).](image)

![FIG. 2: (a) Time evolution of the A1g phonon temperature after excitation with 4.6mJ/cm². The blue dashed line indicates the thermodynamical melting temperature. The average long time laser induced heating is indicated by the red dashed line. (b) Time evolution of the central frequency of the Stokes line for a pump excitation of 4.6mJ/cm². (c) Thermal frequency shift of the A1g phonon at 20 picoseconds after pump excitation versus the pump excitation density and the expected temperature variation. The dashed red line shows the temperature dependence of the frequency shift obtained from continuous wave experiments. (d) Raman response for the unperturbed system (t=-10 ps, black curve), for the ultrafast non-thermal response (t=1ps, red curve) and for the thermal response (t=20 ps, green curve). The left and right panels depicts Raman spectra in the low and high excitation density limit, respectively. (e) Time traces of the intensity of the new phonon line for various excitation densities.](image)

The ratio of the intensity of the Stokes and anti-Stokes spectra allow extraction of the non-equilibrium phonon temperature as a function of time. The evolution of the phonon temperature after the pump excitation with a density of 4.6 mJ/cm² is depicted in Fig 2.a. In the first 3 ps the phonon temperature raises to more than 2000 K. Clearly this does not correspond to a thermodynamic temperature raise, but merely reflects the non-equilibrium phonon occupation which is boosting the anti-Stokes response. On the same timescale, however, also the frequency of the A1g mode softens considerably (see Fig 2.b) to values which are not achievable under equilibrium conditions (at atmospheric pressure). This indicates that not only population effects, but also electronic screening occurs on this timescale. 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 tem-
temperature is reached in about 10 picoseconds after pump irradiation. Based on the equilibrium thermodynamical and optical properties of Antimony, one can estimate the expected temperature raise resulting from the photo excitation. As an example, based on the reflectivity, optical penetration depth, and heat capacity of Antimony, one can estimate the expected temperature raise resulting from the power density of 4.6 mJ/cm² results in a temperature raise of approximately 80K. This is indeed what is observed experimentally, as is indicated by the red dashed line in Fig.2(a). The temperature raise estimated from the intensity of the anti-Stokes signals is confirmed by the frequency shift of the A₁g phonon, as is indicated by the red dashed line in Fig.2(b) which indicates the expected frequency for Sb at T = 370 K [28]. 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 Fig.2(c), which compares frequency of the A₁g 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 [29] (red line). The good agreement of the experimental and estimated temperature (at long times >10 ps) indicates that diffusive heat transport by photo-excited 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 non-thermal nature of the processes occurring at early times following laser irradiation. Firstly the calculated phonon temperature in the first 10 picoseconds reaches values up to 2200 K, well above the equilibrium melting temperature of Antimony (indicated by the blue dashed line in Fig.2(a)). Secondly, the frequency of the A₁g mode in the first 10 picoseconds reaches values lower than those measured under equilibrium conditions at any temperature up to the melting point. The observed non-thermal 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.2(d), where the upper and lower panels show the Raman response in the region of the A₁g mode at different times for low (2.7mJ/cm²) and high (8.4mJ/cm²) excitation density, respectively. Both before arrival of the pump pulse (black traces) as well as at late times (green traces) the phonon response shows the standard Lorentian distribution (L1) for both excitation densities. In contrast, the early time responses (red traces) differ drastically. For moderately low power density (<5 mJ/cm²) the A₁g phonon shifts to lower frequency, keeping a Lorentian 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 strong evidence for this comes from the threshold behavior observed in the activation of the L2 mode as demonstrated in Fig.3(a). The mode is only observed for excitation densities exceeding 5 mJ/cm², and shows a linear increase of intensity upon further increasing the excitation density.

A two component fit of the high excitation density Raman spectra at different delay times reveals that the additional phonon mode, unlike the L1 mode, has a time independent frequency. Moreover, the frequency of the new mode is ~10% lower than the frequency of the equilibrium A₁g mode, and ~20% higher than the E₉ mode. This latter mode, which is active in a different scattering geometry, 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(e).

FIG. 3: (a) Maximum intensity of the new vibrational mode (L2) of the induced phase as a function of pump power density. (b) Sketch of the induced non-linear dynamics in the A7 metals. The curves represent cuts of the free energy for a distortion along the A₁g direction. For low density electronic excitation the minimum of the free energy stays on the fully symmetric (A₁g) direction thereby preserving the A7 symmetry. Excitation densities exceeding 2 electron per 100 atoms (5 mJ/cm²) lead to a symmetry breaking due to displacement along a low symmetry direction (possibly E₉).
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. No anti-correlation between the intensities of the L1 and L2 modes has been observed. This makes it unlikely that the observed new mode is due to a new phase which coexists with the A7 structure. We therefore conclude that both observed modes originate from the optically induced phase, and that this phase has a lower symmetry than the A7 structure. One intriguing possibility is that both observed modes originate from the optically induced phase transition in the A7 metals. The anti-correlation between the intensities of the L1 and L2 sets in (green dashed area in Fig.3 (a) and (b)). As the excitation density is increasing 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 non-thermal low symmetry phase for excitations exceeding 2 electron per 100 ions. Ultrafast symmetry lowering transitions are important for ultrafast bidirectional switching and contrasts most of the observed ultrafast phase transitions to date.

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We have also performed a study of Bismuth, which results completely analogous to those reported in this article on Antimony.

[29] The dispersion relations of the $E_g$ modes in Antimony single crystal[27] show that a doubling of the unit cell would give an additional zone center mode at a frequency close to the observed one.