Chapter 5

Bismuth and Antimony: Toward the Simple Cubic Phase?

5.1 Introduction

Nearly all of the elemental metals crystallize into a cubic (FCC, BCC) or hexagonal closed packed (HCP) structure. An exception to this is found in the elemental crystals of Bismuth, Antimony and Arsenic, which crystallize into the \( \alpha \)-Arsenic structure (A7) with rhombohedral space group R\( \bar{3}m \). The structure of the A7 compounds is shown in Fig.5.1 (a). It can be described as a distorted simple cubic structure, where the (111) planes of atoms have an alternating displacement along the [111] direction. The structural anomaly of the semimetals Bi, Sb, and As has been widely discussed in the past[16, 7], and is found to originate from a strong electron phonon coupling. In one dimension, this type of distortion is the well known Peierls distortion[1]. The ideas leading to the formulation of the theory for the Peierls distortion actually originate from the structure of the A7 compounds and was initially dubbed the Jones-Peierls mechanism[1]. The mechanism is based on the observation that the distortion leads to the presence of two non-symmetry-related sites for the atoms within the unit cell. This, as argued by Harry Jones, introduces a small band-gap in the electronic structure over extended regions of the Brillouin zone which stabilizes the structure: The elastic energy cost for the deformation is compensated by the electronic energy gain due to the opening of the gap (see Fig.5.2 (a)). The presence of the small gap in extended regions of the Brillouin zone is also responsible for the semimetallic behavior of the A7 elemental compounds.[20, 1] For a more detailed explanation see the appendix at the end of this chapter.
From a Raman scattering point of view, the A7 metals are of particular interest. The Peierls distortion from the cubic phase has the same displacement pattern as the Raman active $A_g$ phonon mode in the A7 structure in which the atoms vibrate along the distortion direction (see Fig. 5.4). Intuitively, one immediately understands that this phonon and the Peierls gap are intimately related. In fact, this $A_g$ mode would be the ‘hard’ mode of a hypothetical phase transition from the cubic phase to the A7 structure. Hypothetical, because none of the A7 compounds actually shows this transition, since the transition temperature is higher than the melting temperature of the compounds. With increasing pressure both Bi and Sb approach the primitive simple cubic phase, but no undistorted simple cubic phase has been reported at the thermodynamical equilibrium.[19] The A7 metals thus provide a beautiful playground for studying the intricate interplay between electronic and vibrational degrees of freedom in the Peierls physics. This is particularly true for experiments addressing both electronic and vibrational excitations. Indeed, both Bi and Sb have served as archetypical cases in studies of coherent excitations in absorbing materials. The main observation in transient optical pump-probe reflectivity experiments has been that these materials show a fast reflectivity response which is strongly modulated by a coherent 3.1 THz excitation. The frequency of the intense coherent response is close to the $A_g$ phonon frequency, and has therefore been assigned to coherent excitation of this particular phonon mode.[5, 12] The frequency of the coherent oscillation is, however, not constant in time; it increases upon increasing pump-probe delay. In high pump power experiments[10] it was found that the initial frequency of the oscillation is about 2.5 THz, which, upon increasing pump-probe delay, slowly ($\simeq 5$ps) approaches the value 3.1 THz which is the frequency observed in continuous wave Raman exper-
iments (see section 5.3.1). This effect was originally ascribed to the non-linearity (anharmonicity) of the crystal potential. Generating coherent phonon excitations using an intense pump pulse leads to a large collective atomic displacement. This should allow for the "exploration" of the static crystal potential far from the equilibrium position: The further the atoms are from the equilibrium positions, the more the anharmonic terms of the crystal potential will influence their motion. It has been argued that this induces the observed softening of the oscillation frequency at early times, as well as the increase of the frequency as the amplitude of the coherent motions decreases due to relaxation and dephasing processes.[10] Later, an alternative, more intriguing, explanation for the phonon softening was suggested based on electronic screening of the crystal potential[11]. This second scenario rekindled the hope of accessing a number of intriguing non-equilibrium phenomena arising from the impact of a high-density electron population of the conduction band on the crystal structure. Time resolved x-ray diffraction suggested that intense irradiation could lead to non thermal melting phenomena, due to the electron-phonon interaction induced flattening of the crystal potential after the pump irradiation[20]. More recently the melting scenario was falsified by the suggestion coming from density functional theory calculations, supported by new x-ray diffraction experiments, that a high enough light induced population of the conduction band should lead to a phase transition from the A7 structure toward a more symmetrical cubic symmetry[2]. The suggested mechanism is sketched in Fig.5.2(b): The optically induced population of the conduction band makes the mechanism stabilizing the Peierls distorted structure less effective. When the population of the conduction band increases, the electronic energy gain obtained from distorting the structure reduces until eventually (for a population around 2.7%) the A7 structure is no longer stable, and the crystal undergoes a transition into the undistorted cubic phase.

In spite of the effort devoted so far to distinguish between the two scenarios outlined above, both from the experimental and theoretical side, no consensus has been reached so far. A clear experimental distinction between the two proposed scenarios could come from the actual observation of an induced cubic phase, but unfortunately this has not been observed to date. A second experimental approach is to use an experiment which does not require a coherent lattice excitation to detect the changes in the materials due photo-excitation into the conduction band. This approach is pursued in the current chapter which presents results of a ultrafast time resolved Raman spectroscopy study of Bismuth and Antimony single crystals. This technique is sensitive to transient changes in the crystal structure through transient changes in the spontaneous vibrational Raman response. Two distinct dynamics will be unraveled: A fast non-thermal one occurring in the first few picoseconds after irradiation, and a slower thermal one which lasts for more than 100ps. In addition to this, a simple phenomenological model, based on a
Landau expansion of the free energy, will be presented which is capable of describing both the phonon softening as well as the eventual collapse of the Peierls state upon photo-excitation. Finally, at the end of this chapter some experiments using excitation powers close to the damage threshold will be discussed, which seem to show a periodic phase transition from the Peierls state to presumably a disordered phase.

5.2 Theoretical considerations

As discussed in the previous section, electronic population of the conduction band leads to a destabilization of the Jones-Peierls phase. The DFT calculations by Fritz et al. [3] nicely exemplified this in a quantitative manner. Here, a more simple, phenomenological approach is followed to give a quantitative description of the phonon softening as a function of the dynamical electronic population $n(t)$ of the conduction band, following the approach suggested by Zeiger et al.[4]. Starting from a hypothetical high symmetry cubic structure, the A7 structure arises from a structural phase transition with the amplitude of the displacement of the atoms along the cube’s body diagonal, $q$, (see Fig. 5.1 (b) ) as the order parameter. This corresponds to the atomic displacement associated to the Raman active $A_{1g}$ phonon. In terms of this order parameter, a Landau expansion of the free energy $E(q)$ may be written as:

$$E(q) = -a_0 q^2 + b_0 q^4 + \ldots$$ (5.1)
Where \( n_0 \) is the number of unit cell for unit volume. Note that in this expression the temperature dependence of the coefficients in the expansion is not included explicitly, since this is less relevant for the present discussion. It will be assumed that there is a non-zero order parameter, hence that the system is in the distorted A7 phase. The equilibrium position in the distorted phase is obtained by minimizing the free energy with respect to \( q \), and is given by \( q_0 = \sqrt{\frac{a}{2b}} \). From the equation of motion \( \mu n_0 q \ddot{q} = -\frac{dE}{dq} \), where \( \mu \) is the reduced mass of the vibration \( (\mu = \frac{1}{2}m_X, X=Bi,Sb,..) \) one easily finds the vibrational frequency of the order parameter excitation (the \( A_{1g} \) Raman mode) to be \( \omega_0 = \sqrt{\frac{4a}{\mu}} \).

Optically induced excitation of \( n \) electrons over the Peierls gap results in two additional contributions to the free energy:

i) A term proportional to the number of excited carriers \( n \) to account for the electronic energy. This term can be taken as \( \propto \Delta n \), where \( \Delta \) is the Peierls gap.

ii) A term accounting for the electron-phonon coupling, i.e. to the amplitude of the lattice distortion through the excited electronic population. This term may be written as \( cq^2n \).

Inclusion of these terms in the Landau expansion gives:

\[
E(q) = -an_0q^2 + bn_0q^4 + (\Delta + cq^2)n(t). \tag{5.2}
\]

Obviously, there is now an additional positive quadratic term in the expansion, which will change both the equilibrium structure, as well as the frequency of the order parameter oscillations. When the product \( cn(t) \) is large enough, the equilibrium structure will actually be the cubic phase, rather than the A7 structure. Thus, the population of the conduction band could cause the Peierls gap to collapse, provided that the density of excited charges is high enough. The shape of the free energy Eq.5.2 is depicted in Fig.5.3 as a function of the displacement \( q \) and excited electron density \( n \). The equilibrium position and the frequency of the vibrational mode as a function of the electron population are easily calculated. The new equilibrium position follows from \( \frac{dE(q)}{dq} = -2an_0q + 4bn_0q^3 + 2cq = 0 \) to be

\[
q_n = \sqrt{\frac{a}{2b} - \frac{cn}{2n_0b}} = \sqrt{q_0^2 - \frac{c}{2n_0b}n}. \tag{5.3}
\]

As expected, the equilibrium\(^2\) distortion depends on the number of electrons excited in the conduction band. In the limit of small \( n << \frac{2n_0bq_0^2}{c} \), \( q_n \) depends linearly on \( n \):

\[
q(n) = q_0 - \frac{c}{n_0bq_0^2}n. \tag{5.4}
\]

\(^2\)The term equilibrium here does not refer to a truly thermodynamic equilibrium, but rather to the transient "equilibrium" structure as a function of the conduction band electron density \( n(t) \).
Figure 5.3: Two dimensional potential landscape as a function of the distortion q, and the density of electrons in the conduction band. The red line shows the equilibrium position as a function of the conduction band electron density.

The phonon frequency (in the harmonic approximation) will also depend on the number of electrons as (see Appendix for a detailed calculation):

$$\omega_n = \sqrt{\omega_0^2 - 4c \frac{n}{n_0}}$$  \hspace{1cm} (5.5)

Again, in the low density limit \( n << \frac{n_0 \omega_0^2}{4c} \) the phonon frequency depends linearly on the number of excited electrons:

$$\omega(n)_{n<<1} = \omega_0 - \frac{8c}{n_0 \omega_0^2} n, \hspace{1cm} (5.6)$$

in agreement with earlier results.[3]

### 5.3 Results and Discussion

#### 5.3.1 Conventional Raman experiments

The full representation of the vibrational modes of A7 structure is:

$$\Gamma_{tot} = A_{1g} + A_{1u} + E_g + E_u$$  \hspace{1cm} (5.7)

where the \( A_{1g} \) and \( E_g \) modes are Raman active and the \( A_{1u} \) and \( E_u \) are acoustic modes. The Raman tensor for the \( A_{1g} \) mode has only diagonal components and is expected to be active in a parallel configuration only. In contrast, the \( E_g \) tensor
5.3 Results and Discussion

has both diagonal and off diagonal components, making modes with this symmetry active in both parallel and crossed polarizations. Fig. 5.4 shows polarized room temperature Raman spectra measured in the $a(cc)a$ and $a(cb)a$ polarization$^1$. for an Antimony and a Bismuth single crystal. For Bismuth, the selection rules are fully respected: the $A_{1g}$ mode appears only in the parallel configuration, while the $E_g$ is active in both (black curve in Fig.5.4). In case of Sb the $A_g$ mode, even though less intense, appears also in the cross polarization measurement. This could be due to the presence of some local surface or bulk disorder in the Antimony crystals.

![Figure 5.4: Polarized Raman spectra of Bismuth and Sb single crystals in a parallel (a) and a perpendicular (b) polarization at room temperature. The inset displays a sketch of the atomic motions of the $A_g$ and $E_g$ Raman active modes.](image)

The atomic displacements associated to the Raman active modes are depicted in the inset of Fig.5.4. The $A_{1g}$ phonon corresponds to a displacement of the nuclei along the body diagonal of the “cubic” structure, giving rise to a sort of breathing mode of the (111) planes. This is the order parameter oscillation discussed in the previous section. In contrast, the $E_g$ mode corresponds to a shear vibration of the planes with respect to each other. Even though both modes will be coupled to the electronic degrees of freedom, it seems, in view of the A7 distortion, natural to expect that the $A_{1g}$ mode will be more strongly coupled to the electronic structure, or, in other terms, that the population of this mode will strongly affect

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$^1$We use the Porto notation throughout, where the polarization and geometry of the experiment is given relative to the crystal axis. The first and last letter indicate the direction of the $k$-vector of the incoming and scattered light, respectively, while polarization of these is indicated by the symbols within the brackets.
the electronic properties of the crystal. Vice versa, one expects that excitation of a high density of carriers into the conduction band will lead to a perturbation to this mode as discussed in the previous section. On the contrary, for the $E_g$ mode, that does not change the distance between the planes, the coupling to the electronic degrees of freedom is expected to be much weaker.

### 5.3.2 Initial Results on Bismuth and Antimony

The measurement in real time of the Raman response, in a all optical pump and probe experiment, would shed some light on the lattice behavior in the early time (µ10ps) after laser irradiation in adsorbing materials. The potential landscape with a high density of excited electron will be mapped making use of this powerful technique. Thus the following part of this contribution is going to be centered on first dynamical measurements of the spontaneous Raman response in A7 compounds. Fig.5.5 (a) shows the measurements of the dynamical Raman Raman response for different pump intensity. The measurements were performed in a triple grating monochromator (T64000, Jobin Yvon). The excitation laser was a 80MHz Ti:sapphire laser (Mira 900) lasing in the ps regime. The laser light were filtered with a custom designed optical scheme (for a detailed description see Chapter 4). Making use of a beam splitter the beam is divided into two, one more intense (pump) and a second weaker (probe). The delay between the pump and the probe is controlled through a remote controlled delay line. The pump and the probe beams are recombined with a second beam splitter and coupled into the Raman microscope in a collinear configuration. The scattered light is collected in a back scattering configuration and coupled into the Raman monocromator. A second polarizer, allowing through only the probe polarization, is placed in front of the spectrometer. The fact that the $A_g$ Raman tensor has only diagonal elements allow the polarization selection of the light scattered from the pump and the probe. Fig.5.5(a) clearly shows that the $A_g$ mode shift at lower frequency upon laser irradiation. To quantify the dynamical shift of the mode, the first moment of the excitation is plotted in Fig.5.5(c). The first moment is defined as $\sum \nu I(\nu)$ and give a value of the average frequency of the mode. It appear clear that the mode frequency shift to lower frequency immediately after the pump irradiation.

The higher the pump intensity the larger is the shift observed. In the high fluency limit two different dynamics become visible. Pointing to Fig.5.5(c), the trace relative to a pump intensity of 17mJ/cm$^2$ shows that after the first 10ps the central frequency of the mode relaxes back, bit it doesn’t reach the equilibrium position. It reach a frequency lower than the equilibrium one and stays there for all the time time window investigated. Fig.5.5(b) shows the transient reflectivity traces measured in the same excitation density region. All the reflectivity traces reported are also characterized by two main characteristic dynamics. The fast increase of
5.3 Results and Discussion

Figure 5.5: (a) False color plot of the Pump and probe Raman measurement of the Bismuth $A_g$ mode at different excitation intensity. (b) Typical spectra at different time delays (-10, 0 and 15ps). (c) Transient reflectivity measurements at 780nm. (d) First moment of the Raman of the spectra features in (a). The data are reported with an offset for clarity.

The reflectivity lasts for a time comparable to the autocorrelation between the two pulses and subsequently the reflectivity display a minimum followed by a slow raise lasting for the all time interval measured.

The poor quality of the transient Raman response were due to the small cross section of the $A_g$ phonon in Bismuth. Moreover the relatively low melting temperature and heat conductivity of Bismuth didn’t allow to explore the high intensity dynamics. Piling up effects due to the high repetition rate of the laser didn’t
allow to explore entirely the non equilibrium dynamics. For all this reasons the focus of our research has been moved to the Bismuth “twin brother” crystal, Antimony. As sketched in the introduction, the physical processes underling the semimetallic behavior of Antimony are similar to the one of Bismuth. Nevertheless a few differences in the thermodynamical properties make Sb more suitable for the experiments, Table 5.1 summarizes them. The melting threshold of Sb single crystal and the heat conductance are higher than in Bi, indicating that the non-equilibrium region accessible before piling up effects between successive pulses is expected to be larger. In addition to that the $A_g$ mode of Sb single crystals is at slightly higher frequency and has a larger Raman cross section, making the experiments easier and less time demanding.

Table 5.1: Comparison between some of the physical properties of Bismuth and Antimony.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bismuth</th>
<th>Antimony</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity</td>
<td>$25,52$J/mol K</td>
<td>$25,23$J/mol K</td>
</tr>
<tr>
<td>Heat conductance</td>
<td>$7,93$W/m K</td>
<td>$24,4$W/m K</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>$544.4$ K</td>
<td>$903.78$</td>
</tr>
</tbody>
</table>

Fig.5.6 reports the transient Raman response for excitation intensity between 2.7 and 8.4mJ/cm$^2$. The dynamics observed are similar to those reported in Bismuth. The two distinct dynamics observed in Bi emerge clearer from the Sb measurements. An ultrafast softening of the $A_g$ mode is followed by a slow relaxation lasting for all the time window explored. In order to make these two distinct dynamics more evident in Fig.5.6(b) the same measurements are plotted subtracted of an average of the spectra at a negative time delay.
Figure 5.6: (a) False color plot of the Pump & probe Raman measurements on the $A_g$ mode of Antimony for different pump intensity. (b) False color plot of the Raman spectra for different pump intensities. An average of the negative spectra has been subtracted to make more evident two different dynamics observed on the phonon frequency. The intensity color scale of the two low power measurements is 10 times larger than the high energy ones (blue negative - red positive).
5.3.3 Detailed analysis on Antimony

Increasing the pump intensity the phonon softening in the fast time scale in the first 5/8ps after pump irradiation increases. The same measurements are plotted in Fig.5.8 with the aim of evidencing the differences between the phonon shape for different pump excitation density. When the probe pulse arrive on the sample 15ps before the pump one (Fig.5.8(c)), as expected, no perturbation of the phonon mode is observed at the power investigated. This clearly indicate that the overall heating effects of the pump are small and that in 12ns (the repetition rate of our laser), the heating effects are diffused away from the laser spot. Only the high excitation density spectra (Fig.5.8(c) - blue curve) shows that at the negative time delay the phonon mode displays a small frequency shift (<1cm⁻¹) due to the average heating effects. On the other end, the transient effects result clearly visible on the positive time delay for all the time window investigated. Fig.5.8(a) reveals that increasing the pump power the $A_g$ phonon mode 25ps after the pump irradiation shift to lower frequency.

To quantify these two dynamics the first moment of the spectra are plotted in Fig.5.7. The pump perturbation induces a frequency shift within the first few ps of the phonon mode proportional to the Pump intensity. Fig.5.7(b) depict the frequency shift related to the two dynamics.

Let us first discuss the average shift at the positive delay (25ps). The temperature dependence of the Raman spectra showed that the frequency of both the $A_{1g}$ and $E_g$ modes decrease linearly increasing the temperature[18]. The magnitude of this frequency softening was explained through the thermal expansion that would lead to a phonon softening. On the other hand to explain the strong line-width increase with temperature an additional broadening arising from electron-phonon coupling was necessary. In absolute value the $E_g$ mode was found to be broader than the $A_{1g}$ one at all temperature for both the compounds. The comparison between the line-width at finite and ”zero” temperature $\Gamma_T/\Gamma_{4K}$ shows that the relative increase is larger for the $A_{1g}$ mode. In the analysis proposed the broadening was ascribed to the electron-phonon coupling considered to be a temperature independent constant. A recent optical study[21] demonstrates through the observation of the lowering of the plasmon frequency in temperature that the charge transfer from electron to hole pocket is significant. As shown in Fig.5.7(b), the shift of the phonon frequency at a positive time is found to depend linearly on the pump intensity (red stars). This evidence, together with the slow relaxation observed lead to the interpretation of the ”25ps” phonon shift in terms of a thermally induced shift of the phonon frequency. The higher is the energy released into the system from the pump pulse, the higher is the local temperature expected, and therefore the largest is the phonon shift expected. The relaxation time of this slow dynamic will be dominated by the heat diffusion, too slow for being observed in the time-window explored. An estimation of the temperature raise induced by the
Figure 5.7: (a) Time dependence of the first moment $A_g$ Raman mode for Sb single crystal. The different pump intensity are plotted with an offset for clarity. (b) The maximum ultrafast non-thermal shift (balls) is plotted versus the pump intensity. The dashed line (red in the color version) is the result of a fit to the data with a quadratic function. The average of the thermal shifts at positive times (between 15 and 35 ps) is plotted vs the pump intensity (stars). The thick line (black in the color version) is the result of the calculated shift of the Raman line due to the temperature raise induced by the pump energy (see text).

The pump pulse in the Sb is given by $\frac{dT}{dE_{\text{pump}}} \approx 8 \frac{K \text{cm}^2}{mJ}$. The temperature dependence of the Raman mode is $\frac{d\nu}{dT} \approx 0.012 \frac{\text{cm}^{-1}}{K}$. The two equation together results in an
shift dependence on the excitation power of:

\[ \frac{d\nu}{dE} = \frac{d\nu}{dT} = \frac{dT}{d\nu} = 0.096 \frac{cm^{-1}}{mJ/cm^2} \] (5.8)

The calculated dependence is plotted in Fig.5.7(b) (black line). The good agreement between the observed experimental shift and the calculated one confirms the interpretation of the slow dynamics as a thermal shift due to the heat induced by the pump excitation.

On the contrary, the ultrafast dynamic observed in the first 10ps after pump irradiation cannot be ascribed to a temperature changes into the sample. The thermodynamical constants of Sb clearly show that the temperature required for such a phonon softening are not reachable with the excitation density used. To give a deeper insight into this ultrafast response revealed by the first momenta of the Raman spectra a detailed analysis of the lineshape of the excitation has been performed.

**Time-dependent lineshape of the A\textsubscript{1g} optical phonon**

**Damaging threshold** To gain a deeper understanding on the optically induced phase transition in Bismuth and Antimony, we measured the Raman spectra for pump and probe overlapped in time and space. The results are reported in Fig.5.9 (a). The measurements of the damaging threshold was carried on alternating the pump & probe measurements with an unperturbed measurement. For pump intensity up to 12.5mJ/cm\textsuperscript{2} no permanent damage was observed in the Raman feature. Above this threshold an irreversible changing in the sample was observed. It should be mentioned that the damage produced is not visible under an optical microscope, but it appears in the Raman measurements as an increase in the Raman cross section (+50%) for the A\textsubscript{1g} mode. This suggest that the damage optically induced in this regime could be a order-disorder transition.

**Lineshape** Before discussing the dynamical phonon response let us look back at Fig.5.8(b) and consider the power dependence of the phonon lineshape for pump and probe overlapped in time. Even below the damaging threshold (I<12mJ/cm\textsuperscript{2}) in the first few picoseconds after pump irradiation a dramatic changes occurs in the phonon lineshape and its central frequency. Fig.5.10 depict the lineshape of the Raman response for pump and probe overlapped in time and space. At low excitation densities the A\textsubscript{1g} phonon mode can be nicely fitted with a single Lorentian distribution at all time delay. On the contrary, at high excitation density the response results to have no longer the simple Lorentian lineshape. As depicted in the left panel of Fig.5.10 an additional component at low energy
(L2) become visible. This indicated that, even below the damaging threshold two excitation regimes can be distinguished. The first one, for low excitation density ($I_1 \leq 5 \text{ mJ/cm}^2$), where the Raman response can be described simply by a shift of the $A_{1g}$, and the second one for intermediate excitation density ($5I_1 \leq 12 \text{ mJ/cm}^2$) where a simple phonon shift no longer reproduce the Raman results. For excitation density of $8.4 \text{ mJ/cm}^2$, a fit of the Raman response at different time allowing the central frequency, width, and intensity of both L1 and L2 to vary revealed that the central frequency and width of L2 would vary in time of less than 10% around the central frequency of $138 \text{ cm}^{-1}$. For this reason we propose that the additional component is at a fixed frequency in time.

Figure 5.8: Phonon line shape for different pump intensity for positive (a), zero (b), and negative time delay (c).
Figure 5.9: (a) Pump power dependence of the Raman at zero delay between the pump and the probe. (b) The first momentum for the spectra at different intensity is plotted. The spectra continuously shift toward lower frequency. The damaging threshold is found to be above 12.5 mJ/cm$^2$.

Figure 5.11 showed the fit parameter obtained with a fixed L2 central frequency (138 cm$^{-1}$) and width (8 cm$^{-1}$) and a free L1 (width, intensity and central frequency). Fig.5.11(b) showed the central frequency obtained for the the $A_{1g}$ (L1) phonon. The two dynamics discussed, in the previous section, making use of the first moment of the spectra are confirmed. The $A_{1g}$ phonon (L1) undergo an ultrafast non-thermal softening followed by the relaxation into a thermal state lasting for all the time-window investigated. The thermal softening is confirmed to be linear with the pump power, while the non thermal dynamic confirmed the previously discussed sub-linear behavior. Fig.5.11 (a) depict the time dependent intensity of the L2 Lorentian features for different pump excitation density. It is revealed that L2 gives a contribution to the Raman mode only above the threshold of $\approx 5$ mJ/cm$^2$, while it is not present in the low excitation density limit.

As anticipated in the introduction the phase diagram of Antimony single crystals under pressure is quite complicated and still debated. Increasing the pressure the structure approaches closely at 7 GPa the simple cubic phase. The Raman response in this low pressure regime revealed a continuous softening of the $A_{1g}$ phonon mode from the 153 cm$^{-1}$ at ambient pressure to $\approx 130$ cm$^{-1}$ at 7 GPa. Between 7 and 9 GPa the Raman measurements revealed the appearance
Figure 5.10: Phonon lineshape in the first picoseconds after pump irradiation (t=0). In the right panel the experimental lineshape measured in the low excitation density limit (2.9mJ/cm$^2$) is depicted. The fit is obtained with two lorentian distribution (one for the phonon response and the second, centered at low frequency, to account for the background). The left panel show the experimental phonon response in the high excitation density limit (8.4mJ/cm$^2$). The spectra are no longer reproduced by two lorentian distribution but a third is needed (L2).

of additional lines corresponding to the incommensurate monoclinic host-guest Sb-IV structure[22]. This suggest the coexistence between the Sb-I and Sb-IV phases. Above 9GPa the tetragonal host-guest incommensurate phase SII become stable.[23] This phase is revealed in Raman spectroscopy by the presence of a band composed of 5 additional modes between 80 and 170cm$^{-1}$.

In view of the Peierls physics described in section 5.2, in the low excitation density limit the optical population of the conduction band "acts as applying pressure". i.e. The Peierls physics consists of the electronic energy gain compensating the lattice energy loss in the distortion (\(E_{tot} = E_{lattice} - E_{electrons}\)). In this sense applying pressure will make the lattice stiffer and will increase the cost of the distortion. From the Peierls point of view this will result in the same effects as reducing the electronic energy gain through the population of the conduction band. Clearly the simple physics described in section 5.2 can’t account for all the phases revealed, different structural dynamics not included in the simple model described makes the cubic phase unreachable. Nevertheless, the phase diagram reach of host-guest structure (both Sb-II and Sb-IV are host-guest phases) suggests that localization phenomena and phase coexistence in Antimony single crystal can be energetically favored. In view of this, the coexistence of two different phonon frequency is ascribed to a local collapse of the Peierls gap. In the low intensity limit the population of the conduction band would cause a "delocalized"
Figure 5.11: (a) Time dependence of the intensity of the L2 peak for different pump intensity. A threshold behavior is revealed, the L2 appear only above 5mJ/cm$^2$. (b) Time traces of the central frequency of the L1 mode.

Peierls band collapse. Increasing the electron density could cause a local collapse of the Peierls gap limiting the electronic delocalization. This would explain the coexistence of the two phonon modes observed in the ultrafast Raman response. Further theoretical investigation would be needed to confirm the “physical feasibility” of this new intriguing state.

High excitation density  Fig. 5.12(a) reports the transient Raman response for a measurements just below the damaging threshold (11mJ/cm$^2$). An anomalous modulation of the Raman response is revealed and made more evident by the plot in Fig.5.12(c), where an average of the negative spectra have been subtracted from the response in (a). It should be mentioned that after the measurements the sample resulted damaged in the sense defined earlier: no damage was visible
in an optical microscope, but enhanced Raman activity of the $A_g$ mode revealed a permanent modification of the crystal structure. Fig.5.12(b) shows the Raman response at different times after the pump irradiation. The measurement at different times are reported to make clear the spectral features at different times.

![Figure 5.12](image)

**Figure 5.12:** (a) Transient Raman response for high pump excitation density 11mJ/cm$^2$. The response appear to be modulated with the anomalous periodicity of 7.2ps. (b) The Raman response at different times is plotted with an offset for clarity (the lines in (a), with number associated, indicates the time where the spectra in (b) are taken). (c) Transient Raman, as in (a), subtracted of an average of the spectra at negative times. (d) First moment and integrated intensity of the experimental feature.

The anomalous periodic modulation of the Raman feature remain unexplained at the present date. Fig.5.12(d) shows the calculated first moment and of the
intensity of the Raman scattering feature. It’s clearly visible that the central frequency and the intensity are anticorrelated, the higher the intensity, the lower the first moment of the spectra. To give a tentative explanation of this feature we performed the fit using three Lorentian distributions, one accounting for the background and two to reproduce the equilibrium (L1) and induced (L2) spectral characteristic. As described before the central frequency and width of L2 was kept constant at 138 cm\(^{-1}\) and 13 cm\(^{-1}\). The only parameters allowed to vary were the characteristic of L1 and the intensity of L2. Fig. 5.13 (a) shows that the fit parameters obtained. The extremely good agreement at all time delay is demonstrated by the low and roughly constant \(\chi^2\) (defined as \(\chi^2 = \sum_i \frac{(I_i^{\text{exp}} - I_i^{\text{fit}})^2}{n_{\text{points}} - n_{\text{parameters}}}\)).

Figure 5.13: (a) Fit parameters obtained with the function described in the text. The central frequency of L2 was kept constant at 138 cm\(^{-1}\) with a width of 13 cm\(^{-1}\). The top panel reports the \(\chi^2\) of the fit demonstrating the good agreement between the data and the fit at all time delays. The middle and bottom panels depict the intensity of L2 and the central frequency of L1, respectively. (b) Two dimensional plot of the fit obtained.

The central and bottom panels of Fig. 5.13 (a) plot the intensity of L2 and the central frequency of L1. Following this analysis, the periodic modulation of the the Raman response demonstrates a periodic switching between the two phases. Tentatively, the modulation could be ascribed to the interplay between the two phases. When the electron density exceeds the critical value, domains of the perturbed ("possibly cubic" or disordered) phase could start interacting. The beating between the two phases could be at the origin of the anomalous modulation of the Raman response. Further theoretical and experimental work should be carried out to give fundament to this new intriguing scenario. From the theoretical point of view the relative stability of the two phases should be calculated and the existence of locally distorted configuration equivalent in energy to the
undistorted one should proved. From the experimental point of view the limiting factors of our experiments were two. Firstly, the high repetition rate (80MHz) of the laser used produce piling up effects due to successive pulses allowing us only a partial exploration of the high excitation density limit. Secondly, the experiment with pump and probe at the same frequency (perpendicularly polarized) didn’t allow the analysis of the $E_g$ mode, whose Raman tensor has both diagonal and off diagonal elements. Time resolved Raman experiments with a lower repetition rate and two different colors (pump and probe) would help unraveling the physics underling the anomalous beating observed.
5.4 Conclusions

In conclusion the transient spontaneous Raman response have been measured in Bismuth and Antimony single crystals. On the phonon response two different dynamics were distinguished: a fast non thermal one in the first 10ps is followed by a slow relaxing dynamic lasting for all the time window investigated. The slow response have been proven to be due to the thermodynamical perturbation of the system. The fast non-thermal dynamics was described in terms of a the collapse of the Peierls gap. In the spirit of the Landau theory of phase transition the Jones-Peierls distorted natural phase is considered to be derived from a non thermally accessible cubic phase. The phonon lineshape observed in the fast dynamics revealed the appearance of a new phonon mode at the threshold excitation density of 5mJ/cm². This was interpreted as the evidence of the coexistence between the A7 structure (pushed towards the simple cubic undistorted phase) and a new non-thermodynamic phase possibly due to the local collapse of the Peierls gap. An anomalous periodic modulation of the Raman response for excitation density close to the damaging threshold has been tentatively ascribed to the periodic beating between the two phases. Further investigation are suggested to give fundament to this intriguing scenario.
5.5 Appendix A: The Jones-Peierls mechanism

The Jones-Peierls mechanism is based on the idea that the distorted lattice has a lower frequency, leading to the presence of two non-symmetry-related site for the atoms within the unit cell. The number of orbital states in the new zone is equal to the number of cells, and therefore half the number of atoms. In this picture the symmetry of the distorted lattice ("neglecting the distortion") is that of a face centered cubic lattice. Fig. 5.14 reveals the comparison between the two unit cells and Brillouin zone. In particular, Fig 5.14 (d) depict the the comparison between the Brillouin zone of the simple cubic (SC) versus the face centered cubic (FCC) ones. It is noticeable that the FCC Brillouin zone is inscribed into the SC one. Jones argued that the new surface of discontinuity illustrated in Fig.5.14 (d) is very near to the surface of constant energy surface in the undeformed lattice. This means that in Bi and Sb the Fermi surface would very nearly coincide with the new boundary. This introduces a small band-gap over extended regions of the Brillouin zone and is responsible for the semimetal character of Bi and Sb.

**Figure 5.14:** Sketch of the simple cubic primitive cell (a), with the relative Brillouin zone scaled by a factor $2\pi$ (b). The face centered cubic unit cell is depicted in (c). The Brillouin zone for the SC and FCC cubic cell are compared in (d). See text for the discussion.
5.6 Appendix B: The Phonon frequency from the free energy

To calculate the phonon frequency for a fixed number of electrons excited in the conduction band we Taylor-expand the free energy in the vicinity of the equilibrium position $q_n$.

$$E_{q=q_n}(n) = E(q_n) + E'(q_n)(q - q_n) + \frac{E''(q_n)}{2}(q - q_n)^2 + h\omega. \quad (5.9)$$

The first term of Eq.5.9 is a $q$-independent shift of the energy and will not affect the vibrational frequency. The second one vanishes, being $q_n$ an "equilibrium" position $E'(q_n) = 0$. The only term determining the vibrational frequency is the last one. The equation of motion is:

$$\mu n_0 \ddot{q} = -\frac{dE}{dq} = (4an_0 - 4c_2n)(q - q_n) \quad (5.10)$$

This is the standard harmonic oscillator equation, where the frequency is reported in Eq.5.5.
Bibliography


