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# Lattice dynamics of antimony at high pressure: an *ab initio* study

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We report *ab initio* calculations of the lattice dynamics of antimony as a function of pressure. Analysis of reported Raman data using calculated two-phonon densities of states allows us to weigh the contribution of anharmonicity to the observed broadening upon increase of pressure. We discuss other plausible mechanisms required to account for the pressure dependence of the Raman linewidths.

**Keywords:** antimony; phonons; *ab initio* simulations; anharmonicity

## 1. Introduction

With the exception of phosphorus, the group of the V-B elements exhibits the A7 rhombohedral structure, generated by applying a deformation along the three-fold axis to a cubic primitive lattice, plus a relative displacement of atoms that results in a primitive cell with two atoms [1]. Among these elements, antimony is known for the strongly anharmonic behavior of the crystal lattice, as revealed by Raman and Brillouin scattering, in particular, under pressure [2,3]. The anharmonicity, together with the semimetallic character of their electronic structure and, for heavier elements, the increasing importance of spin-orbit interaction, has hindered so far an accurate investigation of their thermodynamic and lattice dynamical properties by means of *ab initio* calculations. Only very recently, spin-orbit interaction has been taken into account for calculations of these properties in bismuth [4–6].

The lattice dynamics of Sb have been determined in the past by inelastic neutron [7] and Raman scattering (see [2] and references therein). Though the electronic bandstructure has been obtained *ab initio* [8], to our best knowledge no first-principles calculation has been reported for the lattice dynamics.

At  $\mathbf{q} = 0$ , the phonon modes of antimony are divided into two degenerate transverse optic modes of  $E_g$  symmetry, and one longitudinally polarized mode, of  $A_g$  symmetry, beside the three acoustic modes. Both  $E_g$  and  $A_g$  modes are Raman and infrared active.

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Recently, Raman experiments conducted at room temperature in a high-pressure diamond anvil cell reported a softening of 25 and 20% for the  $E_g$  and  $A_g$  phonon frequencies, respectively, i.e. from 110 and 150  $\text{cm}^{-1}$  to 83 and 120  $\text{cm}^{-1}$ , upon increase in pressure up to the transition to an incommensurate host-guest phase near 8 GPa [2]. Similarly, a giant increase in linewidth was observed, from 8.9  $\text{cm}^{-1}$  (5.4  $\text{cm}^{-1}$ ) to 30  $\text{cm}^{-1}$  (17  $\text{cm}^{-1}$ ) for the  $E_g$  ( $A_g$ ) full-width-at-half-maximum between atmospheric pressure and the transition to the first high-pressure phase. This increase of linewidth was found to be fully reversible, and lowering the temperature to 5 K resulted in narrower linewidths at a given intermediate pressure, thus indicating a significant contribution of anharmonic terms of the lattice potential to the spectral linewidths. Very recent inelastic X-ray scattering experiments on antimony allowed us to obtain the pressure dependence of the phonon dispersion relations of antimony and motivated the use of *ab initio* calculations in order to analyze the observed phonon linewidths. The experimental results will be reported elsewhere [9].

We want to address here the origin of the pressure-induced broadening of the Raman peaks by using first-principles calculations of the lattice dynamics. To this aim, we performed *ab initio* calculations of the lattice dynamics with the ABINIT software package [10–12].

The electronic structure of antimony in the  $A7$  ( $R\bar{3}m$ ) phase was calculated using Hartwigsen–Goedecker–Hutter pseudopotentials generated on the basis of a fully relativistic all-electron calculation [13]. Spin-orbit interaction was included in the Hamiltonian, as it was found relevant to adequately describe the specific heat of antimony [14] and the lattice dynamics of other group V-B semimetals like bismuth [4–6]. To this aim, a grid of  $12 \times 12 \times 12$   $k$ -points in the Brillouin zone was used for the integration required for determination of the local charge density, and a plane wave kinetic energy cutoff of 25 Hartrees. The local density approximation to the exchange and correlation energy was employed.

The atomic coordinates, lattice vectors, and lattice parameters were fully relaxed under the constraint of constant pressure between 0 kbar, which corresponds to an equilibrium volume of 58.84  $\text{\AA}^3$ , and the volume threshold above which the structure becomes unstable according to the calculations, 53.5  $\text{\AA}^3$ .

The dynamical matrices corresponding to a grid of  $12 \times 12 \times 12$   $q$ -points were calculated at each pressure point within the framework of density functional perturbation theory and interpolated to obtain the phonon dispersion relations along selected high symmetry directions [11,12,15].

Figure 1 shows the calculated phonon dispersion relations at equilibrium conditions (solid curves) compared with the inelastic neutron scattering (INS) data reported at room temperature [7]. The agreement is especially good for the acoustic branches, which is consistent with the excellent agreement in the calculated heat capacity reported in our previous work [14]. The calculated phonon dispersions at 53.5  $\text{\AA}^3$  are also plotted in Figure 1, displaying as a main feature the softening of optical branches in the region of smallest quasi-momentum, with a minimum at the  $\Gamma$  point. Upon application of pressure, a distinct behavior is observed at the zone boundary depending on the high symmetry direction: whereas for the  $\Gamma$ – $T$  direction, hexagonal axis, all modes show an increase in frequency with increasing pressure, the phonon branches at  $X$ -point display a softening for all acoustic modes and a hardening of the optic modes. Moreover, there is a large increase in frequency with increasing pressure at  $0.5\Gamma X$ , which is consistent with observations performed in metals by inelastic X-ray scattering [16].

Figure 2 displays the calculated densities of states (DOSs) corresponding to a decay channel into two modes, the so-called sum states and difference states, which represent the most common anharmonic decay channels. From the pressure dependence of these two-phonon DOSs we can infer the following information concerning the Raman modes: (i) Upon increase in pressure, the anharmonic decay probability into difference modes increases up to three times. (ii) On the contrary, the decay probability into sum modes decreases dramatically with pressure, due to the softening of the Raman modes. The contribution to the Raman linewidth of these decay channels

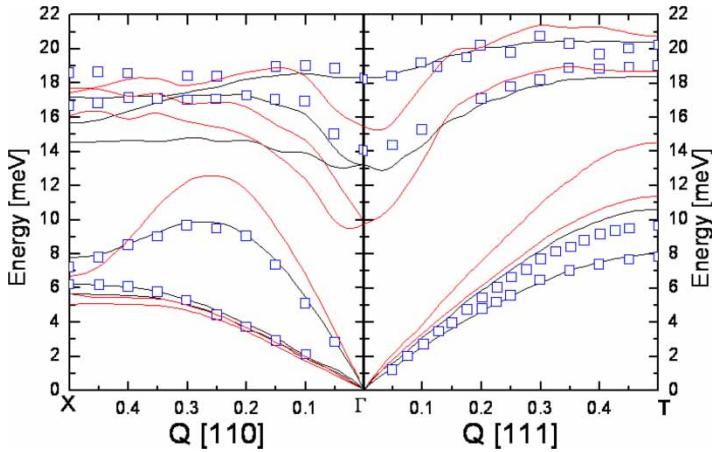


Figure 1. Calculated phonon dispersion relations of antimony at equilibrium (black, solid) and at a volume of  $53.5 \text{ \AA}^3$  (red, solid), compared with INS data at ambient conditions (squares) [7]. The high symmetry directions are labeled according to the hexagonal unit cell (see online for color version of the figure).

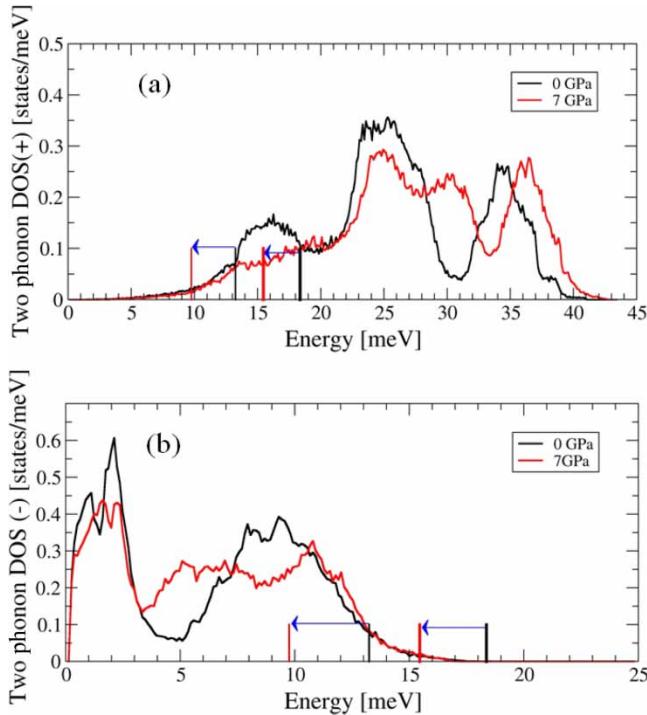


Figure 2. Calculated two-phonon DOSs corresponding to (a) sum and (b) difference processes as a function of pressure. Black curves represent data at the theoretical equilibrium, whereas red curves display data at a volume of  $53.5 \text{ \AA}^3$ , corresponding to a calculated pressure of 7 GPa. The vertical lines indicate the calculated energy of the Raman modes at these pressures (same color code) and the arrows indicate the shift with increasing pressure predicted from the calculations (see online for color version of the figure).

can be calculated using the following expressions [17]:

$$\Gamma_+(\omega) = |V_3^+|^2 \rho_+(\omega) [1 + n_{\text{BE}}(\omega_1) + n_{\text{BE}}(\omega_2)] \quad \text{with } \omega = \omega_1 + \omega_2,$$

and

$$\Gamma_-(\omega) = |V_3^-|^2 \rho_-(\omega) [n_{\text{BE}}(\omega_1) - n_{\text{BE}}(\omega_2)] \quad \text{with } \omega = \omega_2 - \omega_1,$$

where  $|V_3^{+,-}|^2$  are the matrix elements of the third-order anharmonic terms of the lattice potential and  $\rho_{+,-}(\omega)$  the corresponding two-phonon DOSs [18],  $n_{\text{BE}}$  is the Bose–Einstein factor, and the frequencies  $\omega_{1,2}$  must obey the above displayed energy conservation rules. Therefore, difference processes can only account for changes in linewidth occurring at high temperature, whereas sum modes contribute both at low and high temperatures. The pressure dependence shown in Figure 2 allows us to account for the experimental observation of an increase in Raman linewidth at fixed pressure upon increase of temperature [2]. However, the increase in linewidth with increasing pressure observed at low temperature is not compatible with an anharmonic contribution due to the pressure dependence of the two-phonon DOSs. We believe that this increase can be due to a combination of two different contributions: higher-order anharmonic terms of the lattice potential and a pressure change of the matrix elements  $|V_3|^2$ , which can be attributed to non-adiabatic contributions due to electron–phonon coupling. Higher anharmonic terms have been reported to play a role in the Raman linewidth of CuI as a function of temperature [17], though they are usually much smaller than the terms described by the two-phonon DOSs. On the other hand, the reported increase in superconducting critical temperature with pressure may signal an increase in the electron–phonon coupling, and therefore non-adiabatic contributions to the linewidth [2]. Contributions due to disorder-induced effects should not play a major role in view of the reversibility of the observed pressure dependence of the linewidth.

## 2. Conclusion

In conclusion, we have reported here *ab initio* calculations of the lattice dynamics of antimony as a function of pressure, and evaluated the anharmonic contributions to the broadening of Raman modes reported in recent experiments. The calculated phonon dispersion relations are in reasonable agreement with the experimental data, as also shown in a previously reported comparison of derived heat capacity with experimental values [14]. The pressure-induced broadening of the Raman peaks can be partially attributed to a contribution of anharmonic decay channels due to so-called difference processes, though a significant contribution of unknown origin must be added in order to explain qualitatively the observed behavior for low-temperature data.

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