

High-pressure Raman spectroscopy of antimony: As-type, incommensurate host-guest, and bcc phases

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Abstract

The vibrational dynamics of elemental solids that form incommensurate host–guest structures are of fundamental interest. High-pressure Raman scattering has been used to examine the vibrational spectrum of the group-V element Sb up to 33 GPa. A_{1g} and E_g phonons of the ambient pressure rhombohedral A7 phase display a marked decrease with pressure, i.e., prior to the transition to the tetragonal host–guest Sb-II phase at 8.6 GPa, via the monoclinic host-guest Sb-IV phase. The Raman spectrum of the incommensurate host-guest Sb-II phase, has five bands between 80 cm^{-1} and 200 cm^{-1} that increase with pressure. For the bcc structure stable above 28 GPa, we observe one weak disorder-induced band that increases with pressure.

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1. Introduction

The recent discovery of incommensurate host–guest structures in elemental metals under pressure has demonstrated unexpected structural complexity in compressed solids, and has challenged theories of condensed matter [1]. First found in the group-II elements Ba and Sr [1,2], the host–guest structure is also shown to form at high pressures in the group-I elements Rb [3] and K [4], the group-V elements Bi, Sb and As [5–8], and most recently in the transition metal Sc [9]. This structure is composed of a host, and an interpenetrating guest component that is incommensurate with the host along one axis. Several interesting phenomena have been observed in these elemental host–guest structures since their discovery in 1999, including atomic modulation of the host and guest components [6–8], incommensurate-to-incommensurate phase transitions [7,8], and ‘melting’ of guest chains [10]. An effect of site ordering has been studied on Bi–Sb binary alloys [11], which showed the formation of a site-disordered incommensurate host–guest

structure. First-principles calculations have been performed on the host–guest structures of group II and V elements using a commensurate approximant structure to describe their electronic structure [12–14].

The host–guest structures found in the elements are metallic, and some of these are reported to be superconductors with relatively high critical temperatures (T_c of 5.0 K for Ba-IV at 13 GPa, 7.0 K for Bi-III at 3.7 GPa, 3.6 K for Sb-II at 8.5 GPa [15–18]). The coupling of electrons to the low frequency phonon modes found theoretically in the Ba-IV approximant [12] might be responsible for the dramatic increase in T_c in the host–guest phase. The lattice dynamics of these complex structures have not been studied either theoretically or experimentally. On the other hand, recent Raman scattering studies of elemental metals (e.g., Refs. [19–21]) have demonstrated the power of vibrational spectroscopy for studying phase transitions and their complementarity to diffraction experiments. The peculiarities of host–guest structures such as incommensurability and modulation may be better understood by studying their vibrational spectra.

Group-V element antimony shows a rich transition sequence transforming from the ambient pressure Sb-I phase with a rhombohedral A7 structure, common to As, Sb and Bi, to a

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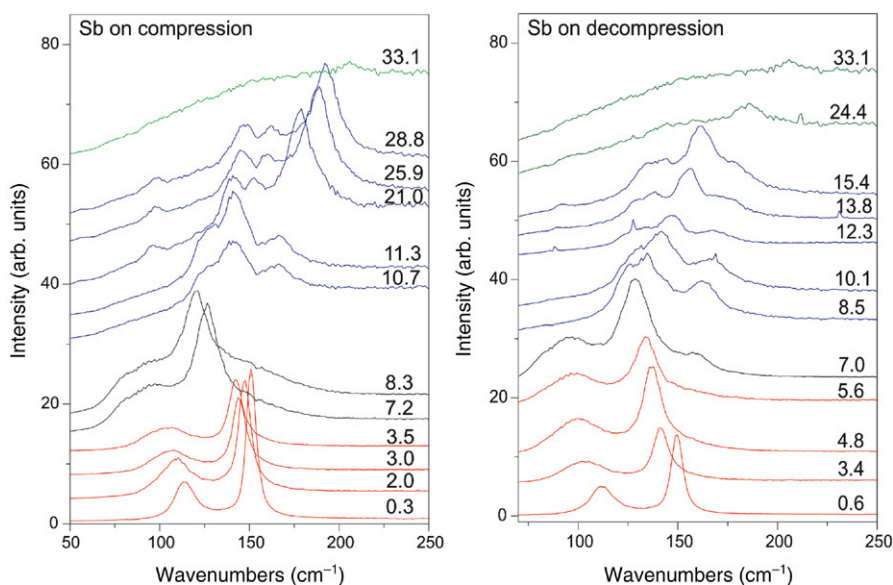


Fig. 1. The Raman spectra of Sb to 33 GPa. The numbers next to the spectra indicate pressure values in GPa. Red coloured spectra correspond to the Sb-I phase, black — to a mixture of Sb-I and Sb-IV, blue — Sb-II, and green — to Sb-III. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

monoclinic incommensurate host–guest Sb-IV phase at pressure of 8.0 GPa, which then transforms at 8.6 GPa to a tetragonal incommensurate host–guest Sb-II phase [6–8]. This finally transforms to the body-centered cubic (bcc) Sb-III phase at 28 GPa [22], an ultimate high-pressure structure for As, Sb, and Bi. There is only limited knowledge of the high-pressure behavior of lattice vibrations in Sb-I, and apparently no Raman data have been reported to date for any of the high-pressure phases of Sb. Here we report the measurements of the vibrational properties of Sb, including its incommensurate host–guest structures [23], up to 33 GPa using Raman spectroscopy.

2. Experimental methods

The experiments were performed on polycrystalline samples of Sb (99.999% purity) loaded in a Mao-Bell piston-cylinder diamond anvil cell. A custom-built high-pressure Raman set-up at the Geophysical Laboratory was used [24]. The Raman spectra were excited with the 514.5 nm line of an Ar-ion laser. The Raman spectra were analyzed by a single-stage spectrograph with a multichannel CCD detector. No pressure transmitting medium was used. Thus, the sample was in direct contact with the culet of a diamond anvil, forming a surface with high optical quality that improves the coupling of the laser beam with the material under pressure. The pressure was determined by the ruby fluorescence method.

3. Results and discussion

3.1. Ambient pressure Sb-I phase

Our Raman spectra of the ambient pressure Sb-I phase with the A7 structure showed two peaks at 114 cm^{-1} and 151 cm^{-1} , in agreement with Refs. [25–28]. With increasing pressure, both modes of Sb-I were observed to decrease in frequency, as can be

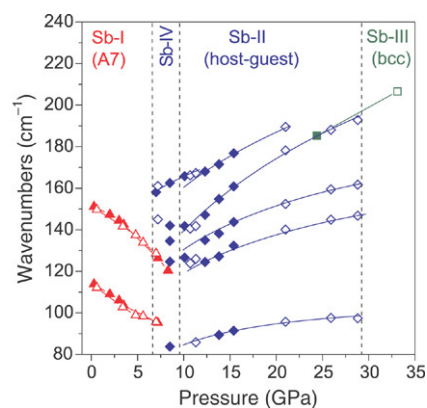


Fig. 2. Pressure dependence of Raman frequencies for Sb. Open symbols denote data collected on pressure increase, and solid symbols — data on pressure decrease. Vertical dashed lines show phase transition pressures.

seen in Fig. 1. The total relative shift for each mode is -16% at 7.2 GPa. The pressure dependence of the two mode frequencies in the A7 phase is shown in Fig. 2, together with the frequencies of the high-pressure phases. The mode-Grüneisen parameters obtained from fitting the data are given in Table 1.

The A7 structure of Sb-I is rhombohedral (space group $R\bar{3}m$), with six atoms per hexagonal unit cell occupying the 6c position (Fig. 3(a)). The structure is a rhombohedral distortion of a simple cubic structure, which forms layers of atoms stacked along the hexagonal axis. This distortion is known to decrease with pressure, with the structure approaching a simple cubic arrangement. The group-theory analysis shows that there are two Raman active modes for the A7 structure, the A_{1g} mode at 150 cm^{-1} and a two-fold degenerated E_g mode at 115 cm^{-1} (Ref. [25]). For phonons propagating along the hexagonal axis (i.e., perpendicular to the layer), the A_{1g} mode belongs to a pure longitudinal motion of the atom planes, while the E_g mode corresponds to the transverse motion.

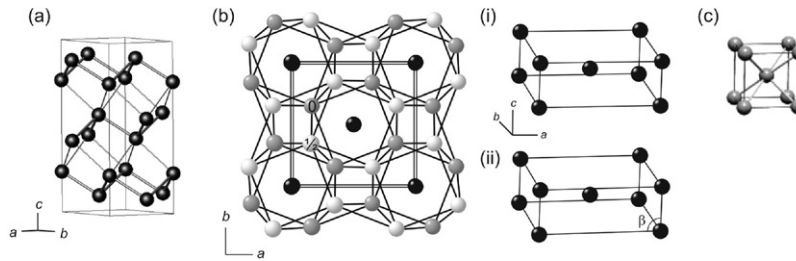


Fig. 3. (a) Crystal structure of Sb-I (hexagonal setting). The shortest Sb–Sb distances are shown by thick lines, outlining puckered atomic layers stacked along the hexagonal c -axis. (b) Host–guest structure of Sb-II and Sb-IV shown in projection down the c -axis, with host atoms shown using light and dark grey symbols, and guest atoms shown using black symbols. Insets show a perspective view of the guest structure of Sb-II (i) and Sb-IV (ii) on the same scale, with the monoclinic angle ($\sim 93^\circ$) indicated for the Sb-IV guest. (c) Crystal structure of the body-centered cubic Sb-III.

Table 1

Observed mode frequencies and average mode Grüneisen parameter for each mode for the Sb-I and Sb-II phases

Sb-I					
Mode	E_g		A_{1g}		
ω_o (cm^{-1})	115		150		
$\bar{\gamma}$	-1.28		-1.29		
Sb-II					
Mode	1	2	3	4	5
ω (cm^{-1}) at 12.3 GPa	88	125	135	147	168
$\bar{\gamma}$	1.24	1.80	2.06	3.05	2.17

The average mode Grüneisen parameter $\bar{\gamma}$ is calculated as $\bar{\gamma} = -(\Delta\omega/\omega_o)/(\Delta V/V_o)$, where ω is the measured frequency and V is the atomic volume taken from Refs. [7,8].

The Raman scattering experiments on the A7 structure in Bi, Sb, and As at moderate pressures up to 0.7 GPa, have shown that both modes soften with increasing pressure [26]. The Raman studies over the entire stability pressure range of the A7 phase in the lighter group-V element As have shown a 17% and 30% decrease in frequency for the A_{1g} and E_g modes, respectively [29]. This observed frequency decrease with pressure agreed with the behavior predicted for the A_g mode on the basis of total energy calculations [30]. Our present data on the Raman frequencies of Sb-I show phonon softening over its whole stability range, and confirm the common trend of phonon softening outlined in previous high-pressure studies for Bi, Sb, and As [26,29].

This pressure-induced zone-center phonon softening in the A7 phase of Bi, Sb, and As is connected with the reduction of the Peierls-like distortion in its layered structure, leading to a semimetal-to-metal transition as well as an increase in electron–phonon coupling and phonon softening. The decrease in the mode frequencies with pressure in this phase appears to reflect the decrease of the intra-layer force constants with pressure, while the increase in sound velocities under pressure in these phases relates to an increase in the inter-layer force constants [26].

3.2. Incommensurate host–guest phases Sb-IV and Sb-II

Above 7.2 GPa, the Raman spectra show the appearance of additional lines, corresponding to the Sb-IV phase in a mixture with the Sb-I phase. The spectra are difficult to analyze because

of the peaks overlap. A single Sb-II phase is observed above 9.0 GPa, and is characterized by five bands, at 88, 125, 135, 147, 168 cm^{-1} at 12.3 GPa, the 147 cm^{-1} band being the most intense one (Figs. 1 and 2). The frequencies of all the bands increase with pressure; notably the most intense peak shows a very large shift relative to the rest of the peaks. The mode Grüneisen parameters are given in Table 1.

The monoclinic host–guest structure of the Sb-IV phase has a 4D space group $I'2/c(\alpha 0\gamma)00$, where the host has $I2/c$ symmetry and 8 atoms in the unit cell occupying the $8f$ positions and the guest has $I2/m$ symmetry and two atoms occupying the $2a$ position [7,8] (Fig. 3(b)). The tetragonal host–guest structure of the Sb-II phase has a 4D space group $I'4/mcm(00\gamma)0000$, where the host has a $I4/mcm$ symmetry with atoms occupying the $8h$ position, and the guest has $I4/mmm$ symmetry with two atoms occupying $2a$ position [7, 8] (Fig. 3(b)). The monoclinic host ($I2/c$) with atoms in the $8f$ position without guest atoms would give three A_g modes and three B_g modes. The tetragonal host ($I4/mcm$) with atoms in the $8h$ position without guest atoms would give one A_{1g} , one B_{1g} , one B_{2g} and one E_g mode. A guest structure ($I2/m$ or $I4/mmm$) with two atoms in the body-centered unit cell would not have Raman-active modes.

A group theoretical analysis is not yet available for these monoclinic and tetragonal host–guest structures. The Raman spectra of the incommensurately modulated structures (not host–guest) are now routinely characterized using procedures derived by Janssen et al. [31,32], where the normal modes are characterized by the irreducible representations of the superspace group. The Raman spectral analysis of “intergrowth” or host–guest structures would require an additional development of this analysis, which to our knowledge is not yet available. On the other hand, the high-quality Raman data obtained in the present work for the host–guest phase of Sb could be used in the future to test the application of such an analysis.

The tetragonal incommensurate host–guest structure of Sb-II is therefore expected to give a rich Raman spectrum, with four modes if only host cell atoms are taken into account. Presence of an additional fifth mode could be explained as originating from the modulation of the host and guest components. Large displacive modulation of the host and guest atoms were reported for Sb-II and IV, causing shifts of atoms up to 0.3 Å from their ideal positions [7,8].

The peculiar larger pressure shift of the most intense 147 cm^{-1} Raman mode of Sb-II in comparison with the rest of the modes could be possibly connected with the pressure dependence of the modulation vector in the host–guest structure. The modulation vector q , defined as a ratio of the c -axis parameters of the host and the guest components ($q = c_H/c_G$), is incommensurate (irrational) and changes smoothly with pressure. In Sb-II, its value decreases from 1.311 at 10.2 GPa down to 1.305 at 25.6 GPa [8]. This pressure shift of the modulation vector appears to affect the pressure shift of the Raman modes.

3.3. High-pressure bcc Sb-III phase

At about 28 GPa, the five bands of the Sb-II phase disappear, and a broad band near 207 cm^{-1} at 33.1 GPa is observed. This change is coincident with the transformation to Sb-III, which has the bcc structure (Figs. 1 and 2). The broad Raman band in this phase is likely to arise from disorder-induced scattering, thus reflecting a maximum in the phonon density of states. The band moves to higher frequencies with pressure. The bcc structure (Fig. 3(c)) with only one atom in the primitive unit cell does not have any Raman-active modes. The pressure shifts of the Raman bands of the Sb-I, II and III phases are reversible upon decreasing the pressure, as shown in Figs. 1 and 2.

4. Conclusions

The frequencies of the Raman-active A_{1g} and E_g zone-center phonons of the ambient pressure phase of antimony (Sb-I) decrease by about 16% with increasing pressure over the phase stability pressure range up to 8.3 GPa. The mode softening is comparable with that reported for the same phase in the lighter group-V element As. Also, for the first time we observed and reported the five Raman-active modes for the metallic high-pressure Sb-II phase, which has an incommensurate host–guest structure and is stable between 8 and 28 GPa. The hardening of the modes with pressure could be connected with the previously observed decrease of the superconducting temperature within the Sb-II phase [18]. Upon the transformation of Sb-II to Sb-III at 28 GPa, the first-order Raman excitations disappear, with only weak and broad disorder-induced scattering observed, consistent with the bcc structure of the phase.

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References

- [1] R.J. Nelmes, D.R. Allan, M.I. McMahon, S.A. Belmonte, Phys. Rev. Lett. 83 (1999) 4081.
- [2] M.I. McMahon, T. Bovornratanaraks, D.R. Allan, S.A. Belmonte, R.J. Nelmes, Phys. Rev. B 61 (2000) 3135.
- [3] M.I. McMahon, S. Rekhi, R.J. Nelmes, Phys. Rev. Lett. 87 (2001) 05501.
- [4] M.I. McMahon, R.J. Nelmes, U. Schwarz, K. Syassen, Phys. Rev. B 74 (2006) 140102(R).
- [5] M.I. McMahon, O. Degtyareva, R.J. Nelmes, Phys. Rev. Lett. 85 (2000) 4896.
- [6] U. Schwarz, L. Akselrud, H. Rosner, A. Ormeci, Yu. Grin, M. Hanfland, Phys. Rev. B 67 (2003) 214101.
- [7] O. Degtyareva, M.I. McMahon, R.J. Nelmes, Phys. Rev. B 70 (2004) 184119.
- [8] O. Degtyareva, M.I. McMahon, R.J. Nelmes, High Press. Res. 24 (2004) 319.
- [9] H. Fujihisa, Y. Akahama, H. Kawamura, Y. Gotoh, H. Yamawaki, M. Sakashita, S. Takeya, K. Honda, Phys. Rev. B 72 (2005) 132103; M.I. McMahon, L.F. Lundegaard, C. Hejny, S. Falconi, R.J. Nelmes, Phys. Rev. B 73 (2006) 134102.
- [10] M.I. McMahon, R.J. Nelmes, Phys. Rev. Lett. 93 (2004) 055501.
- [11] U. Häussermann, O. Degtyareva, A.S. Mikhaylushkin, K. Söderberg, S.I. Simak, M.I. McMahon, R.J. Nelmes, R. Norrestam, Phys. Rev. B. 69 (2004) 134203.
- [12] S.K. Reed, G.J. Ackland, Phys. Rev. Lett. 84 (2000) 5580.
- [13] U. Häussermann, K. Söderberg, R. Norrestam, J. Amer. Chem. Soc. 124 (2002) 15359; U. Häussermann, Chem. Eur. J. 9 (2003) 1472.
- [14] A. Ormeci, H. Rosner, Z. Kristallogr. 219 (2004) 370.
- [15] E.Yu. Tonkov, High Pressure Transformations, A Handbook, Gordon and Beach, 1992.
- [16] J. Wittig, B.T. Matthias, Phys. Rev. Lett. 22 (1969) 634; A.R. Moodenbaugh, J. Wittig, J. Low Temp. Phys. 10 (1973) 203.
- [17] N.B. Brandt, N.I. Ginzburg, J. Exp. Theoret. Phys. 39 (1960) 1554; Soviet Physics J. Exp. Theoret. Phys. 12 (6) (1961) 1082. Engl. Transl.
- [18] J. Wittig, J. Phys. Chem. Solids 30 (1969) 1407.
- [19] H. Oljnyk, Phys. Rev. Lett. 68 (1992) 2232.
- [20] H. Oljnyk, W.A. Grosshans, A.P. Jephcoat, Phys. Rev. Lett. 93 (2004) 255505.
- [21] A.F. Goncharov, V.V. Struzhkin, H.K. Mao, R.J. Hemley, Phys. Rev. B 71 (2005) 184114.
- [22] K. Aoki, S. Fujiwara, M. Kusakabe, Solid State Commun. 45 (1983) 161.
- [23] O. Degtyareva, Acta Cryst. A 61 (2005) C62.
- [24] A.F. Goncharov, E. Gregoryanz, V.V. Struzhkin, R.J. Hemley, H.K. Mao, N. Boctor, E. Huang, High pressure phenomena, in: R.J. Hemley, G. Chiarotti, M. Bernasconi, L. Ulivi (Eds.), Proceedings of the International School of Physics Enrico Fermi, IOS Press, Amsterdam, 2002, p. 297. Course CXLVII.
- [25] R.N. Zitter, J. Phys. Chem. Solids 32 (Suppl. 1) (1970) 285.
- [26] W. Richter, T. Fjeldly, J. Renucci, M. Cardona, in: M. Balkanski (Ed.), Proceedings of the International Conference on Lattice Dynamics, Paris, France, Flarion, Paris, 1978, p. 104.
- [27] M.L. Bansal, A.P. Roy, Phys. Rev. B 33 (1986) 1526.
- [28] A. Roy, et al., J. Phys. Chem. Solids 58 (1997) 741.
- [29] H.J. Beister, K. Strössner, K. Syassen, Phys. Rev. B 41 (1990) 5535.
- [30] R.J. Needs, R.M. Martin, O.H. Nielsen, Phys. Rev. B 33 (1986) 3778; Phys. Rev. B 35 (1987) 9851.
- [31] T. Janssen, J. Phys. C 12 (1979) 5381.
- [32] Th. Rasing, P. Wyder, A. Janner, T. Janssen, Phys. Rev. B 25 (1982) 7504.