Structural, Vibrational, and Electronic Study of Sb_2S_3 at High Pressure

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Supporting Information

S.1. Vibrational properties of Sb_2S_3

In order to understand the lattice dynamics of Sb_2S_3 it is important to remind that the structure of Sb_2S_3 is composed of linked SbS_3E and SbS_5E units, here E refers to the lone electron pair of Sb atoms, since the vibrational modes of chalcogenide compounds have been usually interpreted in a simplified manner in terms of molecular-like units. Within this context, the optical phonons of Sb_2S_3 have been partially interpreted in the past as coming solely from SbS_3 units (without any mention to SbS_5 units) **[1,2]**. The undistorted SbS_3 units, which have an ideal trigonal pyramidal (C_{3v}) symmetry, give rise to four normal modes of vibration: symmetric stretching $\nu_1(A_1)$, anti-symmetric stretching $\nu_3(E)$, symmetric bending $\nu_2(A_1)$, and anti-symmetric bending $\nu_4(E)$. Koudelka *et al.* estimated the frequencies of SbS_3 units from those measured in $SbCl_3$ molecules and found them to be close to 112, 138, 269, and 302 cm^{-1} **[1]**. Following similar arguments, the undistorted SbS_5 units, which have an ideal tetragonal pyramidal (C_{4v}) symmetry, give rise to nine normal modes of vibration: axial stretching $\nu_1(A_1)$, antisymmetric in-plane stretching $\nu_4(B_1)$, antisymmetric in-plane stretching+bending

ν_7(E), symmetric in-plane stretching $\nu_2(A_1)$, antisymmetric in-plane bending ν_8(E), symmetric in-plane bending $\nu_3(A_1)$, anti-symmetric out-of-plane bending $\nu_5(B_1)$, anti-symmetric in-plane bending $\nu_6(B_2)$ and symmetric in-plane bending ν_9(E). Stretching modes in distorted tetragonal pyramidal SbS_5 units (similar to those of stibnite) can be observed for instance in $MnSb_2S_4$, with frequency values around 283 and 300 cm^{-1} **[3]**. Despite pure vibrations of SbS_3 units should display considerable higher frequencies (340-380 cm^{-1}) than those observed in $Sb(SR)_3$ molecules **[4,5]**, the vibrational frequencies of $MnSb_2S_4$ have been previously interpreted as due to SbS_3 units instead of distorted SbS_5 units. These arguments suggest that stretching frequencies around 300 cm^{-1} in undistorted SbS_5 units and above 340 cm^{-1} in undistorted SbS_3 units would be expected, which are consistent with the shorter average Sb-S bond distances in SbS_3 units as compared to the SbS_5 units.

To finish this section and just to give an insight of the complex lattice dynamics of Sb_2S_3, we can mention that both SbS_3 and SbS_5 units are linked in stibnite so they have smaller symmetry than in the ideal configuration. This decrease in symmetry leads to splitting of the doubly degenerated E modes of the isolated units. Furthermore, normal vibrations corresponding to SbS_3 and SbS_5 units get mixed in Sb_2S_3, which makes difficult the assignment of the Raman modes. In particular, the link of SbS_3 units with neighboring SbS_3 and SbS_5 units makes impossible the observation of pure symmetric and anti-symmetric stretching modes of SbS_3 units in Sb_2S_3. According to our calculations, the optical mode with the lowest frequency is a silent mode of A_u symmetry with theoretical frequency near 25 cm^{-1} at room pressure. This mode corresponds to the typical shear mode between alternate layers of layered materials. On the contrary, the two highest optical modes are infrared-active modes of B_{1u} and B_{3u} symmetry corresponding to the mixture of a partial symmetric stretching $\nu_1(A_1)$ of SbS_3 units and axial stretching $\nu_1(A_1)$ of SbS_5 units. In fact, the highest Raman active modes are two pairs of (A_g + B_{2g}) modes, which correspond to partial anti-symmetric ν_3 stretching of SbS_3 units and ν_8 stretching of SbS_5 units together with partial ν_2 bending of SbS_3 units and ν_1 stretching of SbS_5 units, respectively. This mixture of stretching or stretching and bending modes of SbS_3 and SbS_5 units allows us to explain why the maximum frequency of Raman-active modes in Sb_2S_3 is slightly above 300 cm^{-1} and well below 340 cm^{-1}.

S.2. Calculated lattice parameters and atomic coordinates of Bi_2S_3 and Sb_2Se_3.

Table S1. Experimental (exptl) and theoretical (theor) values of atomic positions of Bi_2S_3 at room pressure. Experimental and theoretical lattice parameters are: experiment: a= 11.269(2), b= 3.9717(3) Å, c= 11.129(2) Å (from **Ref. 6**), theory: a = 11.40958 Å, b = 3.9680 Å and c = 11.0068 Å.

Atom	x	y	z
Bi(1)	0.0164(2) (exptl)	0.25 (exptl)	0.6745(2) (exptl)
	0.0149 (theor)	0.25 (theor)	0.6750 (theor)
Bi(2)	0.3406(3) (exptl)	0.25 (exptl)	0.4661(2) (exptl)
	0.3608 (theor)	0.25 (theor)	0.4638 (theor)
S(1)	0.0494(16) (exptl)	0.25 (exptl)	0.1311(11) (exptl)
	0.0476 (theor)	0.25 (theor)	0.1294 (theor)
S(2)	0.3773(17) (exptl)	0.25 (exptl)	0.0604(12) (exptl)
	0.3768 (theor)	0.25 (theor)	0.0554 (theor)
S(3)	0.2165(16) (exptl)	0.25 (exptl)	0.8069(12) (exptl)
	0.2142 (theor)	0.25 (theor)	0.8080 (theor)

Table S2. Experimental (exptl) and theoretical (theor) values of atomic positions of Sb_2Se_3 at room pressure. Experimental and theoretical lattice parameters are: experiment: a= 11.80, b= 3.97 Å and c= 11.65 Å (from **Ref. 7**), theory: a = 11.7968 Å, b = 3.9818 Å and c = 11.2831 Å.

Atom	x	y	z
Sb(1)	0.4971(1) (exptl)	0.25 (exptl)	0.8228(3) (exptl)
	0.5226 (theor)	0.25 (theor)	0.8290 (theor)
Sb(2)	0.3432(1) (exptl)	0.25 (exptl)	0.4559(2) (exptl)
	0.3499 (theor)	0.25 (theor)	0.4624 (theor)
Se(1)	0.7162(2) (exptl)	0.25 (exptl)	0.7105(3) (exptl)
	0.7149 (theor)	0.25 (theor)	0.6966 (theor)
Se(2)	0.5597(3) (exptl)	0.25 (exptl)	0.3673(2) (exptl)
	0.5536 (theor)	0.25 (theor)	0.3667 (theor)
Se(3)	0.3675(2) (exptl)	0.25 (exptl)	0.0629(3) (exptl)
	0.3706 (theor)	0.25 (theor)	0.0521 (theor)

S.3. Pressure dependence of bond-lengths in Bi_2S_3 and Sb_2Se_3.

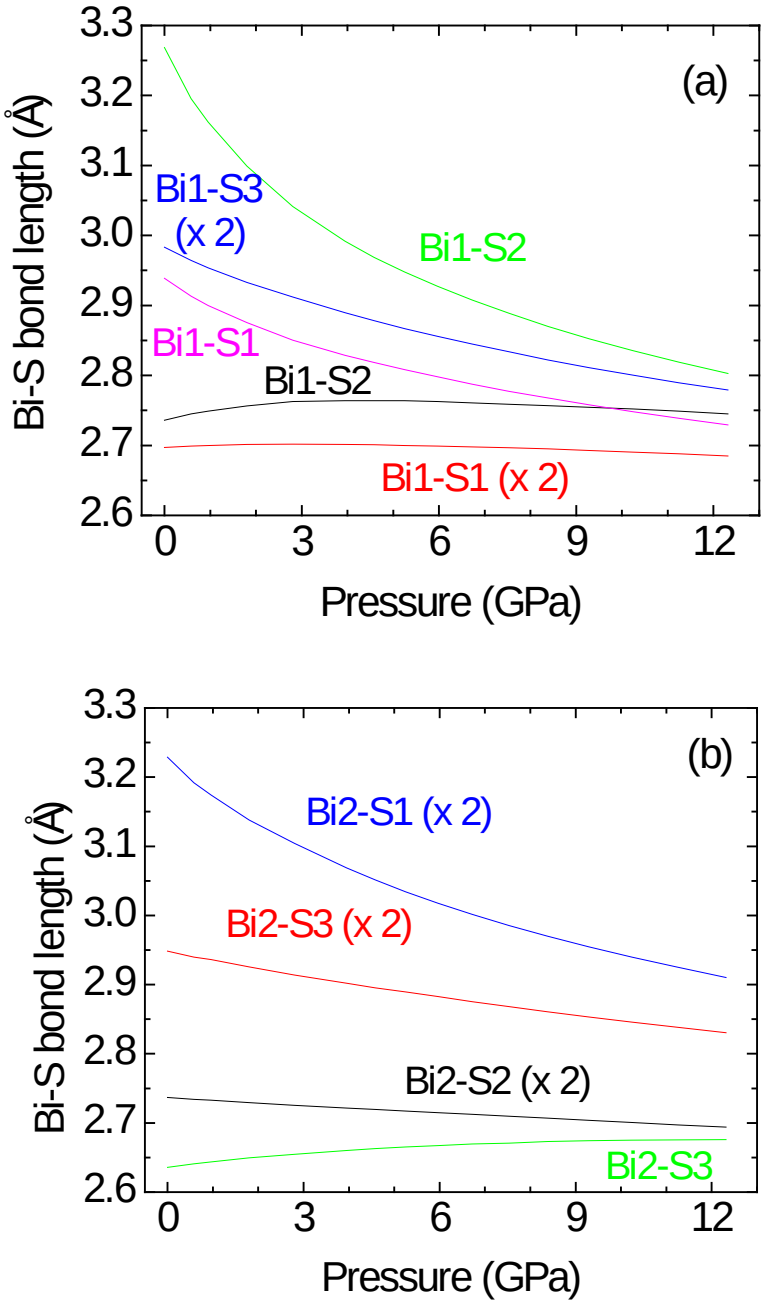

Fig. S1 (a) Theoretical pressure dependence of the Bi(1)-S bond lengths in Bi_2S_3. (b) Idem for the Bi(2)-S bond lengths.

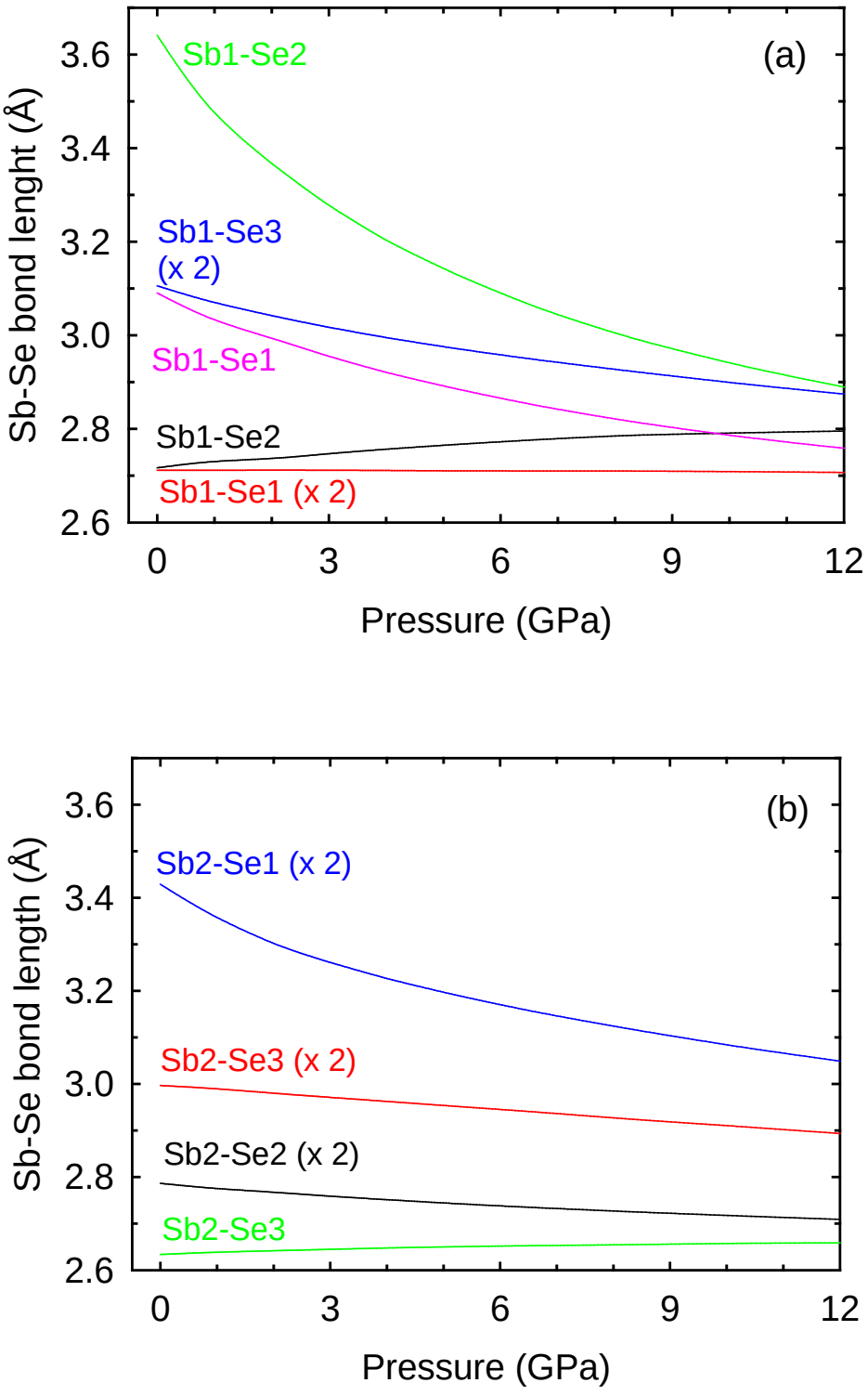

Fig. S2 (a) Theoretical pressure dependence of the Sb(1)-Se bond lengths in Sb_2Se_3. (b) Idem for the Sb(2)-Se bond lengths.

S.4. Pressure dependence of Raman-active modes in Bi_2S_3 and Sb_2Se_3.

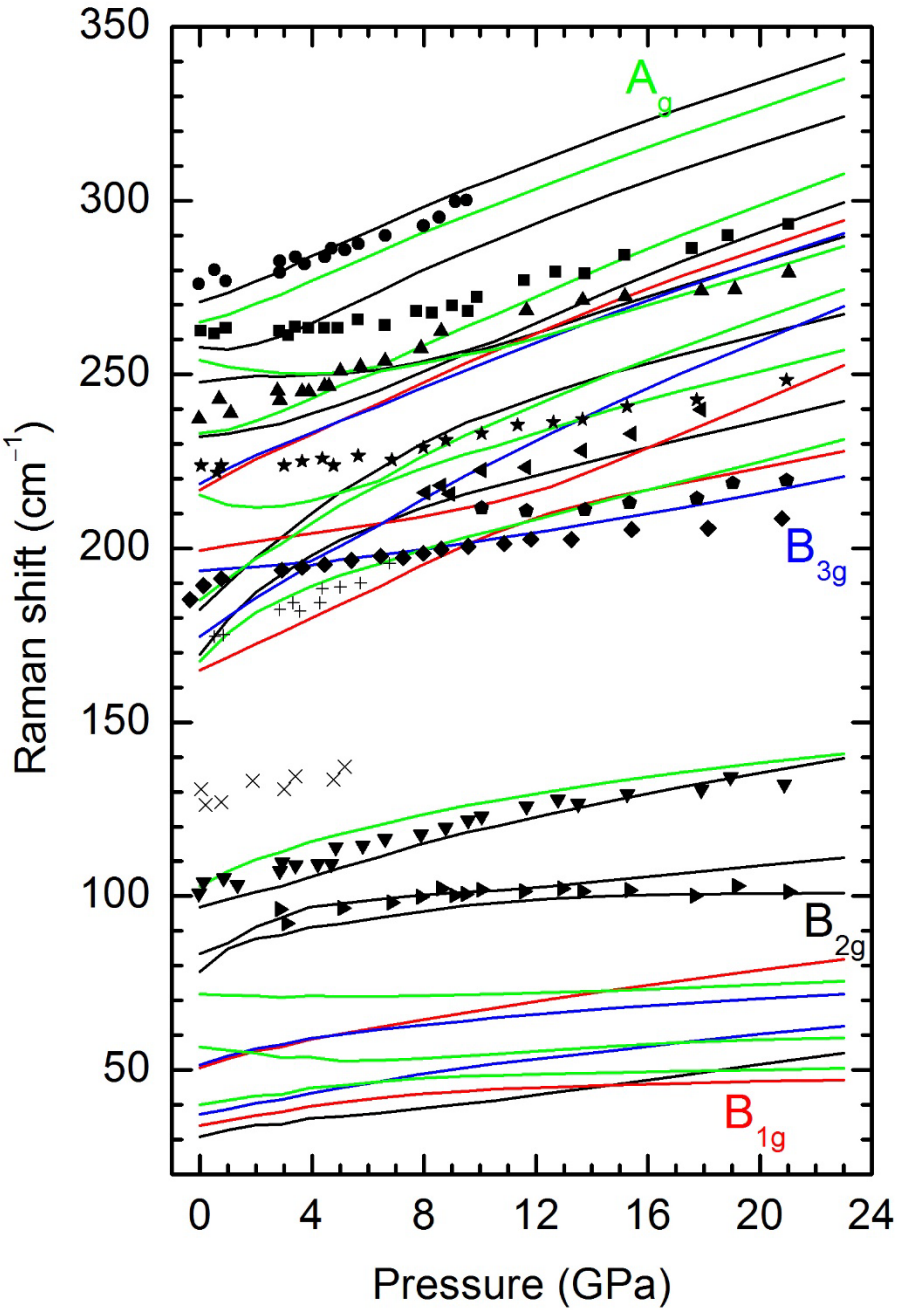

Fig. S3 Experimental (symbols) and theoretical (lines) pressure dependence of the Raman-mode frequencies of Bi_2S_3. Different colors represent Raman-active modes of different symmetries.

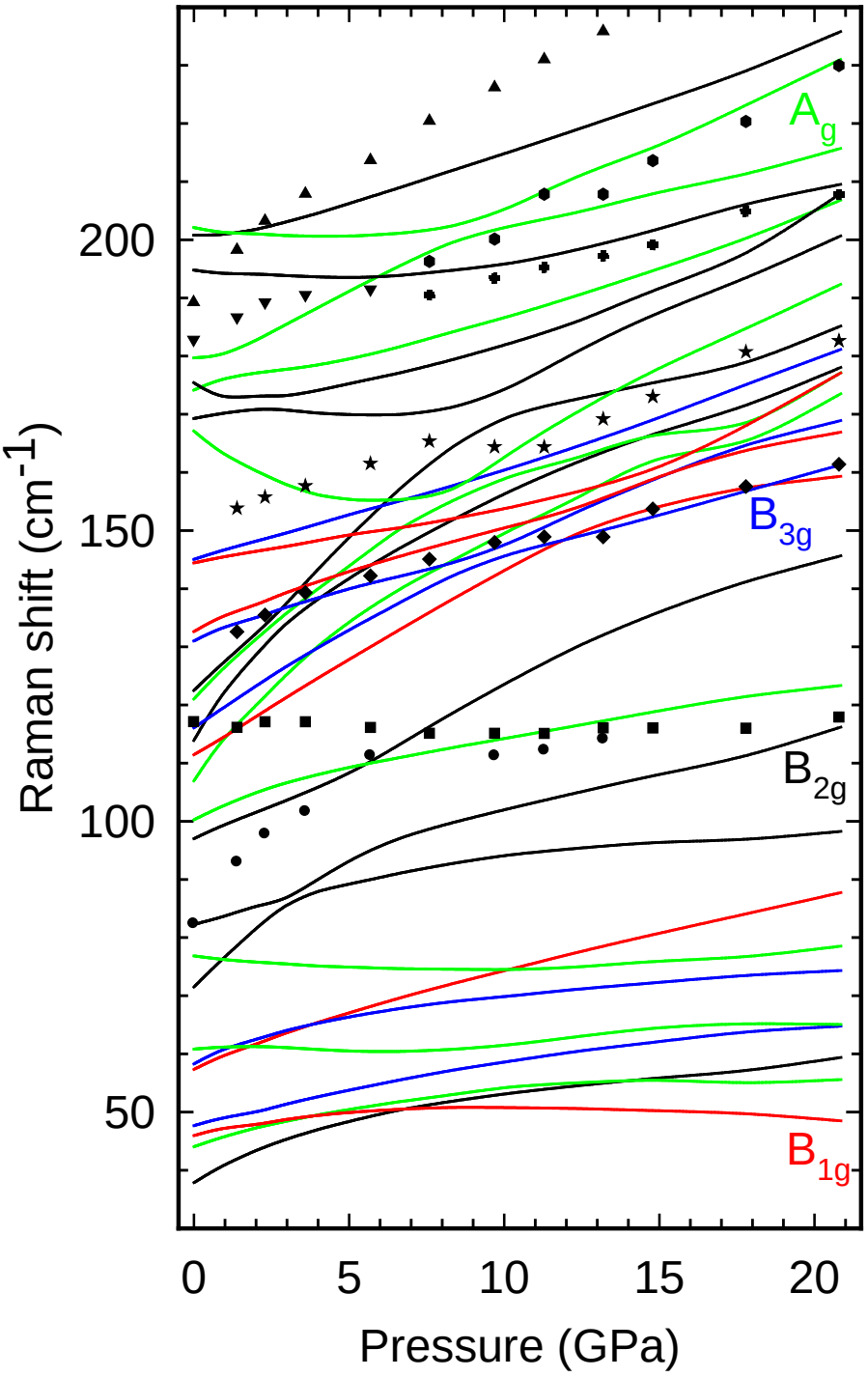

Fig. S4 Experimental (symbols) and theoretical (lines) pressure dependence of the Raman-mode frequencies of Sb_2Se_3. Different colors represent Raman-active modes of different symmetries.

S.5. Pressure dependence of electronic band structure in Bi_2S_3 and Sb_2Se_3.

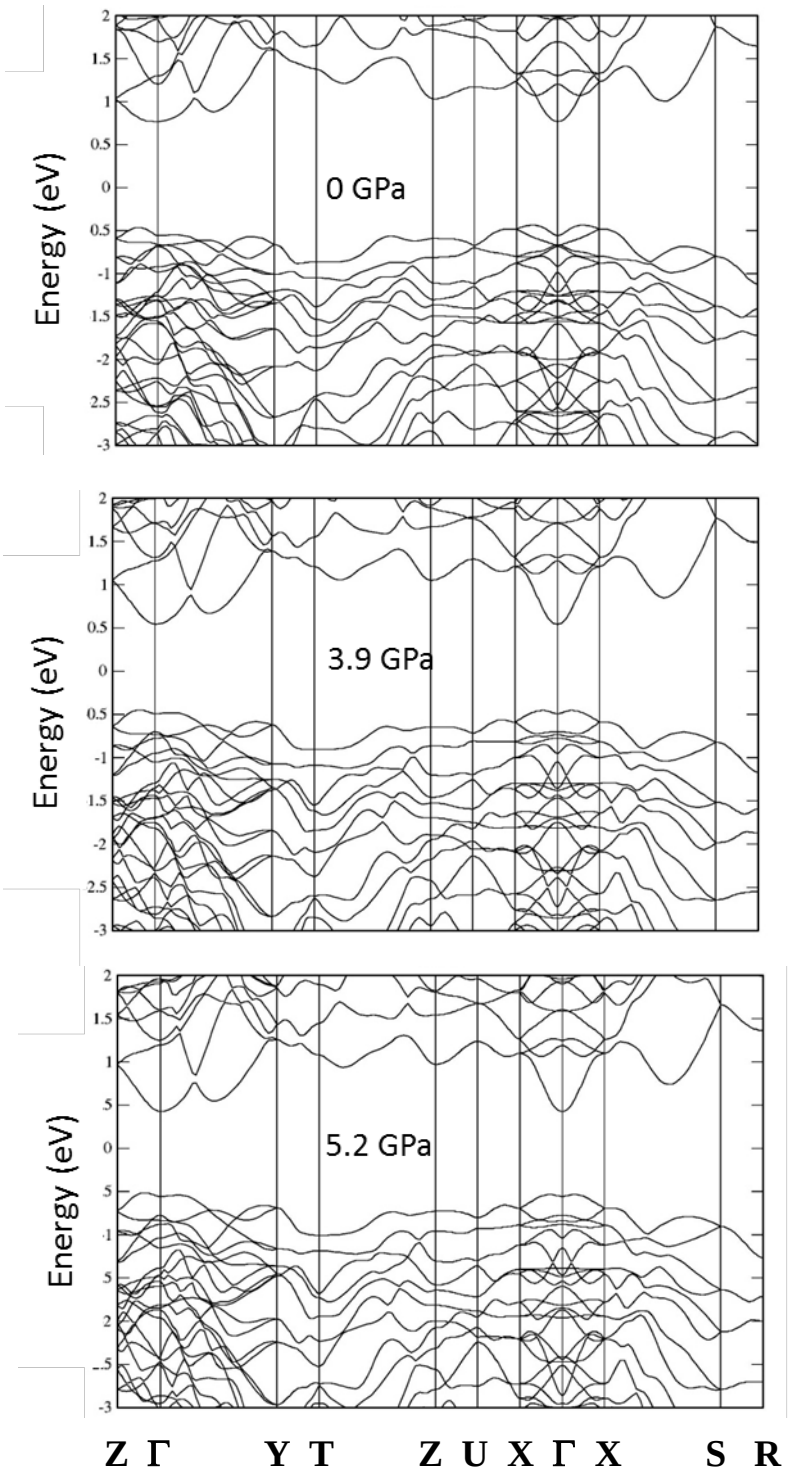

Fig. S5 Calculated electronic band structure of Bi_2S_3 at 0, 3.9 and 5.2 GPa.

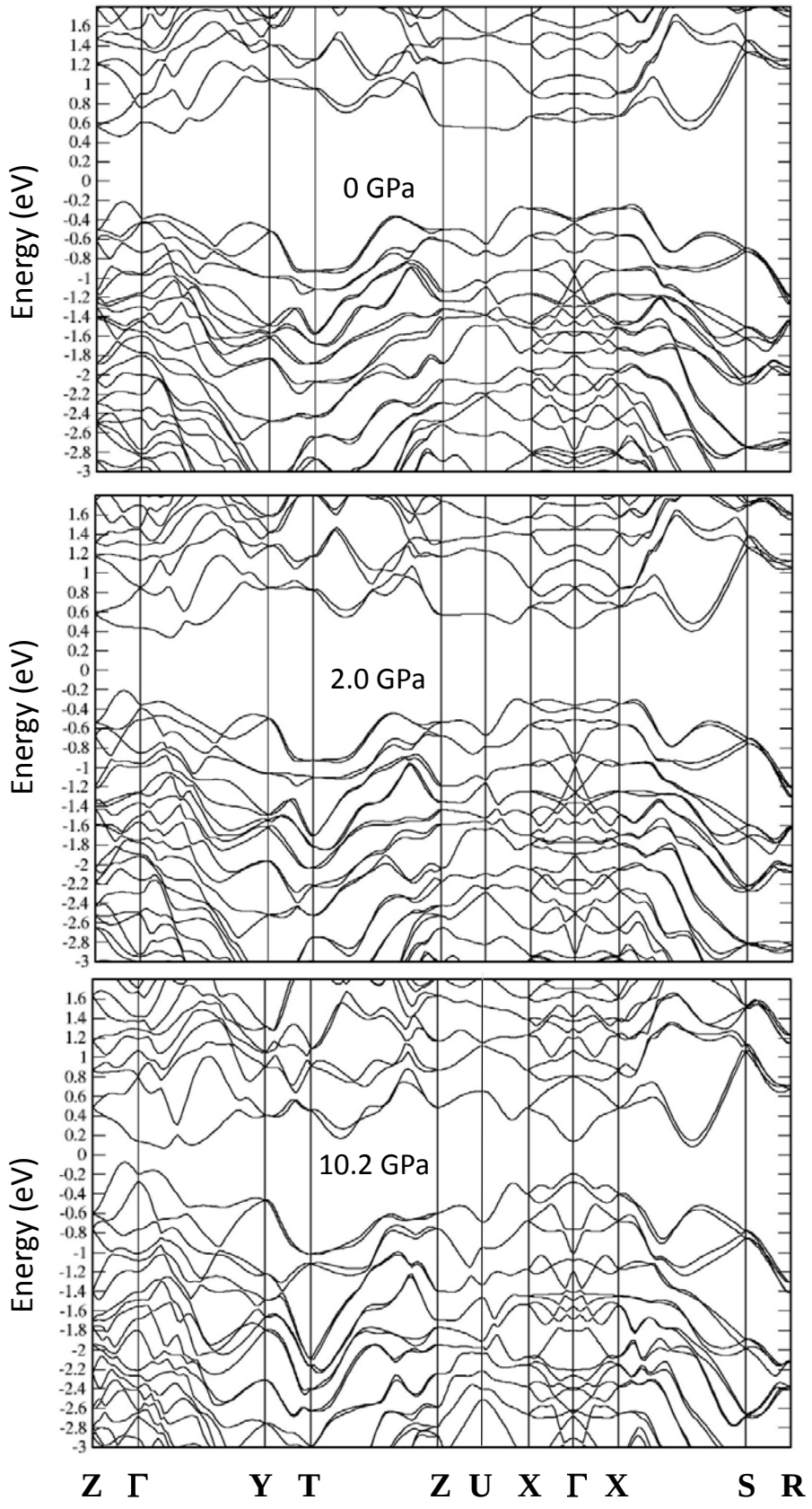

Fig. S6 Calculated electronic band structure of Sb_2Se_3 at 0, 2.0, and 10.2 GPa.

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