Theoretical study of phase transitions in Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$ under compression

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Abstract

We report a theoretical study of Sb$_2$S$_3$, Sb$_2$Se$_3$ and Bi$_2$S$_3$ sesquichalcogenides at hydrostatic pressures up to 60 GPa. We explore the possibility that the R-3m, C2/m, C2/c and the disordered Im-3m phases observed in sesquichalcogenides with heavier cations, viz. Bi$_2$S$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$, could also be formed in Sb$_2$S$_3$, Sb$_2$Se$_3$ and Bi$_2$S$_3$, as suggested by recent experiments. Our calculations show that the C2/m and C2/c phases are energetically unstable for any of the three compounds over the entire range of pressures examined. In contrast, the disordered bcc-like Im-3m phase is energetically stable at high pressures; however, it is only for Sb$_2$Se$_3$ that the disordered phase presents dynamical stability below 60 GPa. Our calculations further show that at ambient pressure the Pnma phase is the most energetically favourable for Sb$_2$S$_3$ and Bi$_2$S$_3$ whereas, and surprisingly, for Sb$_2$Se$_3$ it is the R-3m phase which presents the lowest enthalpy energy at 0 GPa, in contradiction to experimental evidence. From lattice dynamics and elastic tensor calculations we observe that both Pnma and R-3m phases are dynamically and mechanically stable at 0 GPa. These results suggest that the formation of the R-3m phase for Sb$_2$Se$_3$ could be feasible at close to ambient conditions. Furthermore, and to aid the identification of this phase, we provide the theoretical crystal structure (lattice and atomic parameters) and complete infrared and Raman spectra.

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I. INTRODUCTION

Since the identification of the trigonal tetradyminate-like R-3m phases of group-15 sesquichalcogenides (i.e. Sb$_2$Te$_3$, Bi$_2$Se$_3$, Bi$_2$Te$_3$) as 3D topological insulators,$^{1,2}$ the family of A$_2$X$_3$ sesquichalcogenides has attracted a great deal of attention from the scientific community. Three-dimensional topological insulators represent a new class of matter, with insulating bulk electronic states and topologically-protected metallic surface states due to time-reversal symmetry and strong spin-orbit coupling, and present potential interest for spintronics and quantum computing applications.$^3$ Due to this fundamental interest and potential applications, identifying new topological insulators and materials with superconducting properties is currently among the most widely-studied topics in condensed matter science.

Stibnite (Sb$_2$S$_3$), bismuthinite (Bi$_2$S$_3$) and antimonoselites (Sb$_2$Se$_3$) minerals are also group-15 sesquichalcogenides; however, they do not crystallize at room conditions in the tetradyminate-like structure, but in the orthorhombic Z$_2$S$_2$-type (Pnma) structure (Fig. 1.a). Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$ are semiconductors with band-gap widths of 1.7, 1.3, and 1.2 eV, respectively.$^{4,5}$ These materials are used in a wide range of technological applications including photovoltaic solar cells, X-ray computed tomography detectors, fuel cells, gas sensors and for detection of biomolecules.$^6$–$^{12}$

The Pnma structure has been identified as a possible post-post-perovskite phase of (Mg,Fe)SiO$_3$ minerals and of NaFeN$_4$ at high pressure (HP).$^{13,14}$ Thus, the study of Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$ at HP could also provide useful information about the HP behaviour of the ABO$_3$ minerals, which are found in the mantle of the Earth. In this context, initial experimental HP studies of Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$ have shown that the Pnma structure is stable under compression, with first-order phase transitions (PTs) occurring around 50 GPa.$^{15–19}$ Curiously enough, recent HP studies have found that Sb$_2$Se$_3$ becomes a topological superconductor at around 10 GPa and 2.5 K,$^{20}$ exhibiting highly conducting spin-polarized surface states similar to Bi$_2$Se$_3$.$^{21}$ Moreover, three further studies have suggested that several first- and second-order PTs occur for Sb$_2$S$_3$ up to 50 GPa.$^{22–24}$ Furthermore, it has also been suggested that the HP phases of Sb$_2$S$_3$ could be similar to those observed for heavier sesquichalcogenides such as Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$.$^{25}$ Therefore, it is of interest to examine and compare the stability of different structural phases (R-3m, C2/m, C2/c and disordered Im-3m) observed for heavier cation sesquichalcogenides (i.e. Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$) on our three minerals of interest, Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$, and at different pressure conditions.

On the other hand, several theoretical studies performed on the R-3m structure of Sb$_2$Se$_3$ have suggested that this phase should undergo a topological quantum phase transition under compression.$^{26,27}$ In fact, it has been reported that such a topological transition was observed experimentally at 2 GPa.$^{28}$ Furthermore, recent calculations suggest that the tetradyminate-like Sb$_2$Se$_3$
structure becomes a topological insulator at ambient pressure. Consequently, HP studies performed on these group-15 sesquichalcogenides are highly relevant to the research on topological states, therefore possible HP phases of these compounds should be thoroughly evaluated. It is worthy of mentioning, that a recent work performed on Bi$_2$S$_3$ predicts the system to be unstable under compression, and decomposing into another stoichiometric system.

In this work, we report theoretical simulations at 0 K of the $Pnma$ and hypothetical $R-3m$, $C2/m$, $C2/c$ and $Im-3m$ phases for Sb$_2$S$_3$, Sb$_2$Se$_3$ and Bi$_2$S$_3$ (Figure 1), with a view to assessing which, if any, are likely to fulfil either of the stability conditions under hydrostatic pressure.

II. THEORETICAL METHODOLOGY

The structural properties of the different crystalline phases of Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$ were calculated within the framework of density-functional theory (DFT). The Vienna Ab-initio Simulation Package (VASP) code was employed to perform simulations with the projector augmented-wave (PAW) scheme including six valence
The Brillouin-zone (BZ) was sampled with Γ-centered Monkhorst-Pack grids employing adequate meshes for the different structural phases of the three compounds: \textit{Pnma} - 6 × 10 × 6, \textit{R-3m} - 12 × 12 × 12, \textit{C2/m} - 6 × 12 × 6, \textit{C2/c} - 10 × 10 × 8, and \textit{Im-3m} (using a \textit{C2/m} conventional cell) - 6 × 12 × 12.

The disordered \textit{Im-3m} phase is a body-centered cubic (bcc) disordered structure, and has been theoretically predicted and experimentally found for Bi$_2$Te$_3$ in 2011. For sesquichacogenides with A$_2$X$_3$ stoichiometry, the bcc lattice site (2a Wyckoff position) is randomly occupied by 40% of A cations and 60% of X anions. This means that such a structure is a disordered phase with a mixture of cations and anions randomly sharing the same bcc crystallographic position and forming a A-X substitutional alloy. Due to the theoretical difficulty in simulating the disordered \textit{Im-3m} structure, we have used a 9/10-fold \textit{C2/m} structure (formation of 9/10 chemical A-X bonds), as was previously employed for Bi$_2$Te$_3$ and Bi$_2$Se$_3$. Moreover it has been observed that the 9/10-fold \textit{C2/m} structure presents a bcc-like structural order, in agreement with the observed XRD patterns, therefore giving support to employ the calculated intermediate bcc-like monoclinic \textit{C2/m} phase to confirm the experimental presence of the disordered \textit{Im-3m} phase.

Structural relaxations were performed by allowing the atomic positions and the unit-cell parameters to change during the ionic relaxation, at different volume values (compressions). From these we obtain the respective external pressure for the specific applied compression (isotropic volume compression) and hence respective set of crystal structures. The pressure-volume (P-V) curves for all the compounds were fitted to a third-order Birch-Murnaghan equation of state to obtain the equilibrium volume, bulk modulus and, respective pressure derivative. The enthalpy, \( H \), curves were computed by considering the relation, \( H = E + pV \), where \( E \) is the total electronic energy of the system, \( p \) is pressure, and \( V \) is the volume. The analysis and comparison of the \( H \) curves for the different polymorphs can provide insights regarding the thermodynamic stability of each phase for increasing pressure values, up until the studied pressure range (60 GPa).

Lattice-dynamics calculations were performed for the energetically favourable polymorphs at different pressure values, namely the \textit{Pnma} and \textit{R-3m} phases of Sb$_2$Se$_3$ at room pressure, and for the disordered \textit{Im-3m} phases of all three compounds, as explained in detail in Secs. III.B and III.C. The phonon properties were computed by using the supercell finite-displacement method implemented in the Phonopy package, with VASP used as the force calculator. Supercells were expanded up to \( 2 \times 4 \times 2 \) for the \textit{Pnma} phase, and \( 2 \times 2 \times 2 \) for the \textit{R-3m} and disordered phases; to allow the exact calculation of frequencies at the zone center (\( \Gamma \)) and inequivalent zone-boundary wavevectors, which were then interpolated to obtain phonon-dispersion curves and density of states on a uniform 50 × 50 × 50 \( \Gamma \)-centered \( \mathbf{q} \)-point mesh.

To correct for the long-range Coulomb interaction (LO-TO splitting), a non-analytical correction, based on the Born effective-charge tensors and the electronic-polarization component of the macroscopic static dielectric tensor, was applied. These quantities were obtained using the density-functional perturbation theory (DFPT) method implemented in VASP.

Infrared (IR) and Raman spectra were calculated for the ground-state \textit{R-3m} phase of the Sb$_2$Se$_3$ structure by employing the methods described in Ref. and implemented in the Phonopy-Spectroscopy package. The linewidths were obtained by computing the third-order force constants and following the many-body perturbative approach described in detail in Refs. and implemented in the Phonopy software.

Elastic tensors were computed to assess the mechanical stability of the two energetically favourable phases of Sb$_2$Se$_3$ at 0 GPa, namely the \textit{Pnma} and the \textit{R-3m} polymorphs. Respective calculations were carried out by employing the central-difference method, where the unique components of the elastic tensor are determined by performing six finite distortions of the lattice and deriving the tensor elements from the strain-stress relationship. For these calculations, it was necessary to increase the plane-wave energy cut-off to converge the stress tensor adequately, which was achieved by systematically increasing the plane-wave cut-off up until 950 eV. We then further employed the ELATE software to analyse the linear compressibility using the computed stress tensors.

III. RESULTS AND DISCUSSION

A. Structural properties of the \textit{Pnma} phase

The \textit{Pnma} phase of the A$_2$X$_3$ structures are composed by weak stacking interactions which hold the layers along the \( a \)-axis together, which description becomes challenging for conventional DFT functionals. We have compared the equilibrium lattice parameters, bulk moduli and pressure derivatives calculated for the \textit{Pnma} phases of Sb$_2$Se$_3$, Sb$_2$S$_3$ and Bi$_2$S$_3$, with existing experimental and theoretical results found in literature (Tab. 1), to verify the accuracy of our theoretical calculations as a prior step before attempting the study of the HP phases.

By observing Tab. 1 we may find that our calculated lattice paramaters of Sb$_2$Se$_3$, calculated at room pressure (\( a_0 = 11.75 \) Å, \( b_0 = 3.98 \) Å and \( c_0 = 11.30 \) Å), are found to be in good agreement with experimental values.
must mention that the most notable deviation of our calculations from those reported in literature is the crystallographic direction where covalently bonded chains prevail. Detailed results are obtained for the bulk Sb₂S₃ system as well as for the Sb₃Te₃ and Bi₂S₃ systems. We note that calculations performed on Bi₂S₃ by employing the Armiento and Mattsson 2005 parametrized GGA functional (AM05) and also with PAW-PBEsol calculations of Ref. 18,57 seems to a slightly better reproduction of c₀ with respect to experimental measurements.18

The last two rows of Tab. 1 show the calculated B₀ and B'₀ results of the Pnma phase of the three compounds and respective comparison to experimental measurements and other calculations. The calculated values obtained by fitting the P-V curves of Sb₂Se₃ to a third-order Birch-Murnaghan equation are B₀ = 31.1 GPa (B'₀ = 6.6), which is close to the experimental values of B₀ = 30 GPa (B'₀ = 6.1) from Ref. 15 and B₀ = 32.7 GPa (B'₀ = 5.6) from Ref. 61.

For Sb₂Se₃, we have obtained B₀ = 31.5 GPa (B'₀ = 6.6), which is within the range of experimental values,18,22,24,57 and also with PAW-PBEsol calculations of Ref. 18. Moreover, these results are also close to those experimentally measured for the As-doped stibine mineral.66

Finally, our values for Bi₂S₃ result in B₀ = 42.3 GPa (B'₀ = 6.8), which is consistent with DFT data16,61 and experimental values reported in Refs. 62, 16 and 19.

### B. Energetic Stability

Since our calculations on the Pnma phases were found to be in good agreement with the overall data found in literature, we have proceeded in carrying out a theoretical study of the hypothetical R-3m, C2/m, C2/c and disordered Im-3m phases of Sb₂S₃, Bi₂S₃ and Sb₃Te₃ to probe whether such phases could be energetically competitive under hydrostatic pressure. Figs. 2a, 2b and 2c show the pressure-dependence of the enthalpy differences, relative to the stable phase at ambient pressure, between the five above mentioned phases of Sb₂S₃, Bi₂S₃ and Sb₃Te₃, respectively. Values of the predicted transition pressures between the different phases are summarized in Tab. II.

From the enthalpy plots (Fig. 2) we may observe that:

| a₀ (Å) | Sb₂Se₃ | Sb₂S₃ | Bi₂S₃ |
|-------|--------|-------|-------|
| Theo. | Exp.   | Theo. | Exp.  |
| 11.80 | 11.80  | 11.27 | 11.30 |
| 11.52 | 11.79  | 11.02 | 11.31 |
| 11.91 | 11.30  | 11.08 | 11.58 |
| 3.98 | 3.83  | 3.96 |

| b₀ (Å) | Theo. | Exp. | Theo. | Exp. | Theo. | Exp. |
|-------|-------|------|-------|------|-------|------|
| 3.99 | 3.97 | 3.81 | 3.84 | 3.97 | 3.97 |
| 3.96 | 3.99 | 3.84 | 3.84 | 3.94 | 3.98 |
| 11.30 | 10.91 | 11.01 |

| c₀ (Å) | Theo. | Exp. | Theo. | Exp. |
|-------|-------|------|-------|------|
| 11.28 | 11.65 | 11.23 |
| 11.22 | 11.79 | 11.24 |
| 11.70 | 11.23 | 11.05 |

| V₀ (Å³) | Theo. | Exp. | Theo. | Exp. |
|---------|-------|------|-------|------|
| 531.1 | 547.1 | 486.0 | 498.3 |
| 511.8 | 547.5 | 487.7 | 469.1 |
| 598.1 | 552.5 | 488.2 | 510.1 |

| B₀ (GPa) | Theo. | Exp. | Theo. | Exp. |
|----------|-------|------|-------|------|
| 31.5 | 32.7 | 32.0 |
| 38.7 | 37.8 | 36.6 |

| B'₀ | Theo. | Exp. | Theo. | Exp. |
|-----|-------|------|-------|------|
| 6.4 | 6.7 | 6.2 |
| 5.6 | 7.9 | 6.4 |
| 5.5 | 7.6 | 6.4 |

This table summarizes the calculated equilibrium lattice parameters (a₀, b₀, and c₀), equilibrium bulk moduli (B₀), and pressure derivatives (B'₀) of the Pnma phase of Sb₂Se₃, Sb₂S₃ and Bi₂S₃. Values are compared to experimental and other theoretical results found in literature.
FIG. 2: Calculated enthalpy vs pressure curves, for the different possible phases (shown in Fig 1) of Sb$_2$S$_3$ (a), Bi$_2$S$_3$ (b) and Sb$_2$Se$_3$ (c), relative to the lowest-energy phase at ambient pressure: the Pnma phase for Sb$_2$S$_3$ and Bi$_2$S$_3$ and the R-3m phase for Sb$_2$Se$_3$.

TABLE II: Theoretical estimation of the pressure-induced phase transitions of R-3m → Pnma and Pnma → disordered Im-3m for the Sb$_2$Se$_3$, Sb$_2$S$_3$ and Bi$_2$S$_3$ compounds (presented in units of GPa).

| Compound | R-3m → Pnma | Pnma → Im-3m |
|----------|-------------|--------------|
| Sb$_2$Se$_3$ | 4.78        | 21.07        |
| Sb$_2$S$_3$  | –           | 35.12        |
| Bi$_2$S$_3$  | –           | 30.08        |

1. At 0 GPa the orthorhombic Pnma phase is energetically stable for Bi$_2$S$_3$ and Sb$_2$S$_3$; however for Sb$_2$Se$_3$ it is the trigonal R-3m phase the most favourable phase at 0 GPa.

2. The two monoclinic C2/c and C2/m phases do not become energetically competitive with the ground-state phase, over the range of pressures examined, in any of the three compounds.

3. The bcc-like disordered Im-3m structure, which can be understood as a disordered solid solution of atoms, is the most energetically stable phase at pressures above 35, 30 and 21 GPa for Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$, respectively.

With respect to the first point, referring to Bi$_2$S$_3$ and Sb$_2$S$_3$, our calculations predict that the Pnma structure is energetically the most stable phase throughout the whole range of studied pressures, as expected from experimental evidences that show the observation of respective phase, both at ambient and at high pressure. Surprisingly, however, our simulations indicate that the R-3m phase of Sb$_2$Se$_3$ is the most stable phase at pressures below 4.8 GPa, being both Pnma and R-3m phases energetically competitive between 0 and 4.8 GPa. This feature contradicts the experimental findings of Sb$_2$Se$_3$ consistently crystallizing to the Pnma phase at ambient conditions. We must note however that at 0 K and 0 GPa, the energy difference between the two phases is only 22.71 meV (per f.u.), which is lower than the thermal barrier ($k_BT \sim 25$ meV at 300 K) required for the phase transition to occur under ambient conditions. In order to probe whether the vibrational contributions to the free energy could alter the energy ordering between the two phases, we have further plotted the free energies, where the entropy terms are obtained from our lattice dynamics calculations, and which will be discussed in more detail in Sec. III C.

Regarding the second point, our analysis further shows that for the three studied compounds, the two monoclinic C2/c and C2/m phases are never energetically competitive up until 60 GPa. These results are compatible with the fact that no phase transition had previously been observed in Sb$_2$S$_3$, Bi$_2$S$_3$ or Sb$_2$Se$_3$ under compression up to ~50 GPa. However, three recent studies have reported low-pressure phase transitions occurring for Sb$_2$S$_3$. A transition to an unknown phase was observed around 15 GPa and several other transi-
tions were also evidenced between 10 and 25 GPa, and tentatively proposed to be the R-3m, C2/c and C2/m structural phases. It must however be clarified that this latter study applied an ethanol-methanol mixture as the pressure-transmitting medium, therefore there is a possibility that the observed transitions could have been induced by non-hydrostatic pressure effects.

Finally, as for the third point, from a thermodynamic point-of-view our results indicate that the bcc-like disordered Im-3m phase, initially identified for Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$, seem to be energetically favourable at HP for our three materials of interest. These results are consistent with the observation of such a phase at around 50 GPa for Sb$_2$Se$_3$ and above 25 GPa for Sb$_2$S$_3$. However, for the Bi$_2$S$_3$ structure, our results do not agree with those found in Refs. 16 and 19, where disorder has been observed above 50 GPa although attributed mostly to a pressure-induced amorphization. Moreover, a more recent work claims that Bi$_2$S$_3$ is unstable above 31.5 GPa, decomposing into a mixture of BiS$_2$ and BiS compounds.

In summary, the agreement of our results regarding the observation of the disordered Im-3m phase for Sb$_2$Se$_3$ and Sb$_2$S$_3$, but not for Bi$_2$S$_3$, suggests that thermodynamic stability is not sufficient to explain the lack of the HP disordered phase for the latter compound. In the following section we discuss the dynamical stability of the Im-3m phase as a function of pressure in order to provide a deeper understanding regarding this question.

C. Dynamical Stability

Energetic stability is a necessary, but not sufficient condition for a structural phase to be synthetically accessible. One should also probe the dynamical stability of the system, which requires the study of the phonon frequencies. If imaginary frequencies emerge (usually represented by negative frequencies in the phonon dispersion curves), this would indicate that the system is at a potential-energy maximum (transient state), undergoing a phase transition and thus cannot be kinetically stable at the given temperature and/or pressure conditions.

In this section, we consider the phonon properties of different phases for the three compounds, which were observed to be energetically the most favourable (Fig. 2) at different pressure values, namely:

1. The disordered Im-3m phases of the three materials at different pressure ranges.
2. The Pnma phase of the three systems at 50 GPa.
3. The Pmna and R-3m phases of Sb$_2$Se$_3$ at 0 GPa.

1. The Disordered BCC-Type Im-3m Phase

To assess the possibility of dynamical stability for the disordered Im-3m phases of the three compounds at HP, we have evaluated the phonon dispersion curves at pressure values of 30 GPa, which is close to the transition pressures observed in Fig. 2; and at higher pressures of 50 (Sb$_2$Se$_3$) and 60 GPa (Sb$_2$S$_3$, Bi$_2$S$_3$).

As illustrated in Fig. 3, at 30 GPa all three disordered structures show negative modes along the dispersion curves, thus indicating that these structures are dynamically unstable at this pressure range.

At 60 GPa the phonon dispersion curves of Sb$_2$S$_3$ and Bi$_2$S$_3$ present imaginary modes (Fig. 3), indicating that neither compound is likely to adopt this phase for pressures, at least until 60 GPa. We note however that the dynamical instabilities found for Sb$_2$S$_3$ and Bi$_2$S$_3$ both decrease (the negative modes shift to higher frequency values, towards positive values) with increasing pressure, suggesting that these phases could in principle become stable at pressures above 60 GPa. In this context, we must note that Efthimiopoulos et al., 16 had observed a pressure-induced amorphization above 50 GPa for Bi$_2$S$_3$, however the authors were not able to identify the phase to be the disordered Im-3m structure, even at 65 GPa. On the other hand, experimental data for Sb$_2$S$_3$, suggests that the disordered bcc-like phase exists between 28.2 and 50.2 GPa. However, it must be noted, that experimental measurements detailed in Ref. 24 were carried out under non-hydrostatic behaviour, due to the employed pressure-transmitting medium.

Finally, our calculations suggest that Sb$_2$Se$_3$ becomes dynamically stable already at 50 GPa; a result that is in agreement with the Im-3m phase being observed experimentally around 50 GPa.

To close this point, we can speculate that the stability of the disordered solid solution of sesquichalcogenides seems to be related to the size of cations and anions since the Im-3m phase is consistently being observed at HP for sesquichalcogenides with heavier cations and anions (Sb$_2$Se$_3$, Sb$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_2$Te$_3$). It seems that the possibility of occuring such a HP phase could be related to the radii size of Se, Te, Sb and Bi (atomic radii: $r_{Se}$ = 117, $r_{Te}$ = 137, $r_{Sb}$ = 141 and $r_{Bi}$ = 182 pm, respectively). Stemming on these values, we can infer that the solid solutions are energetically favourable in sesquichalcogenides if the atomic radii of the cation and anion differ by less than ~ 65 pm, or if the size ratio between them is smaller than 1.55 (case of Bi$_2$Se$_3$). It is thus likely that the disordered Im-3m phase of Sb$_2$S$_3$ could indeed stabilize, because the radii difference between $r_{Sb}$ and $r_{S}$ is 37 pm (141-104=37 pm) and the size ratio is 1.35, and therefore within the above mentioned thresholds. However, the larger radius of Bi results in a larger radii difference (78 pm) and ratio (1.75) with respect to S, which could therefore evidence the instability of such a disordered phase for Bi$_2$S$_3$ at HP.

Moreover and as suggested in Ref. 36, the atomic radii between the anion and cation tends to become approximately equal under pressure due to a higher probability of charge transfer from cation to anion. Therefore, HP inherently creates a favourable enviroment for the disor-
FIG. 3: Simulated phonon dispersion curves of the disordered bcc-like Im-3m phases of Sb$_2$S$_3$ (a), Bi$_2$S$_3$ (b) and Sb$_2$Se$_3$ (c), and calculated at 30 GPa (left) and 50 (Sb$_2$Se$_3$) or 60 GPa (Sb$_2$S$_3$ and Bi$_2$S$_3$; right). The BZ $\mathbf{q}$-vector description represents the $C2/m$ space-group, according to the symmetry of the employed cell.

ordered phase due to the decrease of the difference between cation and anion atomic radii. Consequently, the transition to the Bi$_2$S$_3$ disordered solid solution could probably be induced for very high pressure values, namely when the difference between the two radii decreases below 65 pm and the ratio decreases below $1.55$.

2. The Low-Pressure Pnma Phase at High-Pressure

In order to study the dynamical stability of the well known low-pressure Pnma phase at HP, we present in Fig. 4 the phonon dispersion curves of the respective phase for Sb$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$Se$_3$ at 50 GPa.

Curiously enough, we find that for Sb$_2$S$_3$ and Bi$_2$S$_3$ the system is still dynamically stable at 50 GPa, although thermodynamically it is not the most stable phase (Fig. 2). These results, together with the dynamical instability observed for the disordered phase of Sb$_2$S$_3$ and Bi$_2$S$_3$ at 50 GPa (Fig. 3), and the thermodynamical instability of the $C2/m$ and $C2/c$ phases, suggest that only the Pnma structure should be observed at 50 GPa for both compounds; up to a plausible phase-transition should occur at higher pressures values.

For Sb$_2$Se$_3$ however, we note that at 50 GPa the Pnma structure starts presenting negative frequencies, localised around the zone-centre, therefore evidencing dynamical instability at the same pressure range where the disordered Im-3m phase is already dynamically stable (Fig. 3). Therefore, our dynamical and thermodynamical results of Sb$_2$Se$_3$, clearly suggests that at HP a transition from the Pnma phase to the disordered Im-3m phase is likely to occur, in good agreement with experiment.
3. The Low-Pressure Phases of Sb$_2$Se$_3$

By considering the enthalpy energies of the $Pnma$ vs $R-3m$ phases of Sb$_2$Se$_3$ (Fig. 2) we have shown that the $R-3m$ phase is energetically the most favourable phase up to $\sim$4.8 GPa, evidencing a very low energy barrier between the $Pnma$ phase of only 22.71 meV (per f.u.) at 0 GPa.

In order to verify if the entropy contributions to the DFT total energies could affect the energetic stability found for $R-3m$ with respect to $Pnma$ (the experimentally observed phase), we have evaluated the constant-volume (Helmholtz) Free energy at 0 GPa (Fig. 5, top). The Helmholtz Free energy ($F$) is obtained by summing the lattice energy (DFT total energy) and the vibrational contributions from the population of the harmonic phonon energy levels.

From Fig. 5 (top), we may observe that at 0 GPa the $R-3m$ phase is the most stable phase at any temperature range, and no transitioning is observed to the $Pnma$ structure. At 0 K, the Free energy difference between the two phases is 27.24 meV, which is $\sim$4.53 meV higher when compared to the enthalpy energy difference at 0 K (zero-point energy). Moreover, at 300 K the energy difference between the phases has a negligible increase of 0.11 meV (27.35 meV).

Another factor that can influence in the ordering of two competing phases is the thermal expansion. Variation of the lattice volume due to thermal expansion/contraction can be introduced by the quasi-harmonic approximation (QHA), in which the thermal expansion of the lattice is obtained from the volume dependence of the phonon frequencies. The evaluation of the equilibrium volume and Gibbs free energy ($G$) at a finite temperature is thus
obtained by minimising the Helmholtz Free energy for a given (constant) pressure. The theoretical background of the QHA is detailed in Refs. 75 and 76 and therefore will not be extended in the present work.

Fig. 5 (bottom) shows the difference of $G$ between the two phases of interest. One may observe that by taking into account the thermal expansion, the $R\text{-}3m$ phase still remains the most stable phase with respect to the $Pnma$ phase, with an energy difference of 29.43 meV at 0 K (very similar behaviour to that obtained from $F$). At room temperature (300 K) the energy difference between the phases decreases slightly down to 26.96 meV. In summary, at room pressure, our Free energy results show that $R\text{-}3m$ is always more stable than $Pnma$ at any temperature. Neither for $F$ nor for $G$ do the differences decrease below the $k_B T$ limit, and therefore the energy barrier is higher than that required for the phase transition to be spontaneous given the available thermal energy (which does not occur when the zero-point energy is not considered).

We also present the $G$ differences of $\text{Sb}_2\text{Se}_3$ for pressure values between 0 and 5 GPa (Fig. 6), in order to analyse the energetic ordering between the two phases and probe if a pressure-induced phase transition could be observed as a function of temperature. We observe that the $R\text{-}3m$ phase persists in the energetically stability at any temperature range up to 1000 K, for 3 and 4 GPa. However we must note that the energy differences between the two phases decreases considerably for increasing pressures and at high temperature values. At 4 GPa the lowest energy difference ($\sim 3.25$ meV) between the two phases occurs between 650-700 K. Increasing the pressure slightly (4.2 GPa) results in an energy decrease of $Pnma$ nearly reaching the energy of $R\text{-}3m$ at around 400 K. In fact, at 4.3 GPa the phase transition from $R\text{-}3m$ to $Pnma$ is observed around 400 K; at 4.5 GPa the transition temperature decreases to $\sim 200$ K. Finally at 5 GPa, the $Pnma$ phase becomes the most energetically favourable structure for the $\text{Sb}_2\text{Se}_3$ system.

Based on the analysis from $G$, we conclude that the pressure-induced transition between the $R\text{-}3m$ to $Pnma$ is favoured at low pressures (between 4.2-4.4 GPa) near room temperature conditions. This conclusion is very similar to that evidenced from the enthalpy plots at 0 K (Fig. 2) where the phase transition is predicted to be around 4.8 GPa.

After confirming that in fact the $R\text{-}3m$ phase is thermodynamically more stable than the $Pnma$ phase at 0 GPa, at any temperature range, we probe the dynamical stability of the $R\text{-}3m$ compound in order to assess whether this structure could potentially be synthesized for $\text{Sb}_2\text{Se}_3$ at/or close to ambient conditions.

For this purpose, we have evaluated the phonon band dispersion and density of states (DoS) of the $R\text{-}3m$ phase phase at 0 GPa, for different temperature values (Fig. 7). We also present the phonon band structure and DoS for the $Pnma$ phase for sake of comparison. Our results show that there are no imaginary frequencies throughout the whole of the Brillouin-zone, thus indicating that both phases to be dynamically stable under ambient conditions (0 GPa and room temperature) and confirming that, as implied by the energetics comparison, both phases could potentially coexist.

In this context, we must note that our results confirm a recent theoretical work performed on the $R\text{-}3m$ $\text{Sb}_2\text{Se}_3$ phase reporting the phonon dispersion curves, and confirming dynamical stability of this phase at 0 GPa and 0 K. In this work, the formation energies of $\text{Sb}_2\text{Se}_3$ were also computed evidencing the $R\text{-}3m$ phase to be dynamically stable. Moreover, $ab\ initio$ molecular dynamics confirm that the $R\text{-}3m$ phase remains unchanged at finite temperature (300 K), once again favouring our presented results.

D. Mechanical Stability

Mechanical or elastic stability is the third condition that should be satisfied for a system to be potentially synthesized. Such a study is carried out by probing if the elastic constants obey the Born stability criteria when the solid is submitted to homogeneous deformations.

We therefore evaluate the mechanical stability of the $Pnma$ and $R\text{-}3m$ phases of $\text{Sb}_2\text{Se}_3$ by calculating and comparing the elastic tensors between the two low-pressure phases (Tab. III).

To confirm the accuracy of our calculated elastic constants, we have computed the linear compressibility of both phases at 0 GPa using the ELATE analysis tools. For both phases, only directions corresponding to positive linear compressibilities were obtained, indicating both phases to be mechanically stable under ambient conditions. In the case of the $R\text{-}3m$ phase, we have obtained linear compressibilities between $\beta_{\text{min}} = 4.9$ TPa$^{-1}$ (hexagonal a-axis) and $\beta_{\text{max}} = 19.5$ TPa$^{-1}$ (hexagonal c-axis) with an anisotropy value of 3.95. For the $Pnma$ phase, the compressibilities fall between $\beta_{\text{min}} = 3.7$ TPa$^{-1}$ (b-axis) and $\beta_{\text{max}} = 25.7$ TPa$^{-1}$ (a-axis) with an anisotropy of 6.87. These values are of the same order as the experimental axial compressibilities of the $Pnma$ phase of $\text{Sb}_2\text{Se}_3$ ($\beta_a = 15.2$ TPa$^{-1}$, $\beta_b = 3.9$ TPa$^{-1}$, $\beta_c = 8.3$ TPa$^{-1}$). We must stress that the bulk modulus of the $Pnma$ phase of $\text{Sb}_2\text{Se}_3$ calculated from the elastic-constant tensor (31.8 GPa), and summarized in Tab. IV together with other elastic moduli, is similar to that obtained from the Birch-Murnaghan fit (c.f. Tab. I), as expected, thus demonstrating the adequate convergence criteria employed throughout the present calculations. The calculated elastic constants in Tab. III fulfill the necessary and sufficient Born criteria for the mechanical stability of orthorhombic (Eq. 1) and rhombohedral (Eq. 2) systems, respectively. Therefore, our calculated elastic constants indicate that both the $R\text{-}3m$ and $Pnma$ phases of $\text{Sb}_2\text{Se}_3$ are mechanically stable under ambient conditions.
FIG. 6: Gibbs free energies of the R-3m phase (green) relative to the Pnma phase (red) of Sb$_2$Se$_3$ as a function of temperature, and for different pressure values.

TABLE III: Calculated elastic constants $c_{ij}$ (GPa) of the Pnma and R-3m phases of Sb$_2$Se$_3$ at 0 GPa.

| $c_{ij}$ | Pnma |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| $c_{11}$ | 30.92 |  |  |  |  |  |  |
| $c_{22}$ | 81.65 |  |  |  |  |  |  |
| $c_{33}$ | 55.20 |  |  |  |  |  |  |
| $c_{12}$ | 17.32 |  |  |  |  |  |  |
| $c_{13}$ | 15.10 |  |  |  |  |  |  |
| $c_{23}$ | 26.89 |  |  |  |  |  |  |
| $c_{44}$ | 17.83 |  |  |  |  |  |  |
| $c_{55}$ | 25.21 |  |  |  |  |  |  |
| $c_{66}$ | 7.69 |  |  |  |  |  |  |

| $c_{11} = c_{22}$ | $c_{33}$ | $c_{12} = c_{13}$ | $c_{15} = -c_{25} = c_{46}$ | $c_{44} = c_{55}$ | $c_{66}$ |
|---|---|---|---|---|---|
| 90.81 | 40.21 | 25.85 | 21.61 | -12.00 | 25.10 | 32.48 |

We note that elastic tensors of Sb$_2$Se$_3$ have been pre-
FIG. 7: Quasi-harmonic phonon dispersion curves for \textit{Pnma}-Sb$_2$Se$_3$ (top) and \textit{R-3m}-Sb$_2$Se$_3$ (bottom). The color gradient runs from blue (low T) to red (high T) across the temperatures associated with the volume expansions considered in our calculations.

Previously calculated,$^{52}$ although as for the bulk modulus, respective components were overestimated as well. We believe a reason for the disagreement could be due to the low cut-off energy used in those calculations.

E. Lattice Parameters, Infrared and Raman Spectra of the \textit{R-3m} phase of Sb$_2$Se$_3$

Our calculations show that the \textit{R-3m} phase of Sb$_2$Se$_3$ is energetically competitive with the \textit{Pnma} phase and is both mechanically and dynamically stable, all of which suggest this phase should be a ground-state structure under ambient conditions.

The inconsistency found between the theoretical and experimental data regarding Sb$_2$Se$_3$, can be based on the possibility that the \textit{Pnma} phase forms faster than the \textit{R-3m} phase, under the usual synthesis conditions. In fact, the \textit{R-3m} phase has not been proposed on the pressure/temperature phase diagram prepared by Pfeiffer et al.$^{79}$ although this study did not attempt to vary the synthesis conditions at close to ambient pressure, as the present calculations suggest. In any case, it is noteworthy of mentioning that our calculations indicate the \textit{R-3m} phase of Sb$_2$Se$_3$ is energetically competitive with the \textit{Pnma} phase at close to ambient conditions. This raises the possibility that the \textit{R-3m} phase could potentially be prepared under slightly non-equilibrium conditions. We must note that Bera et al.$^{28}$ have claimed of having observed such a phase at room temperature, although such an observation has not been confirmed by any other experimental group up until now.

In order to assist with the possible experimental synthesis of this phase, we provide the calculated lattice parameters and atomic positions of our optimised zero-pressure \textit{R-3m} structure in Table V.

We have also computed the IR and Raman spectra to aid in the identification of the spectral signatures that should distinguish the \textit{R-3m} from the \textit{Pnma} phase (Fig. 8).

The frequencies, irreducible representations and IR/Raman intensities associated with each of the zone-centre (\textGamma-point) vibrational modes are listed in Table VI.

The inversion symmetry in the \textit{R-3m} structure leads to mutual exclusion between the IR and Raman activity of the modes, with each spectrum being characterised by four bands.$^{25}$ The most intense Raman band occurs around 139 cm$^{-1}$ ($E_g$), while a second prominent feature is predicted at $\sim$204 cm$^{-1}$ ($A_{1g}$). The frequency of

| Site | Sym. | x   | y   | z   |
|------|------|-----|-----|-----|
| Sb$_1$ | 6c   | 0.00000 | 0.00000 | 0.60082 |
| Se$_1$ | 3a   | 0.00000 | 0.00000 | 0.00000 |
| Se$_2$ | 6c   | 0.00000 | 0.00000 | 0.78792 |

TABLE V: Predicted lattice constants and atomic positions for the hexagonal unit cell of the \textit{R-3m} phase in Sb$_2$Se$_3$ at 0 GPa.

| Site | Sym. | x   | y   | z   |
|------|------|-----|-----|-----|
| Sb$_1$ | 6c   | 0.00000 | 0.00000 | 0.60082 |
| Se$_1$ | 3a   | 0.00000 | 0.00000 | 0.00000 |
| Se$_2$ | 6c   | 0.00000 | 0.00000 | 0.78792 |

TABLE VI: Calculated vibrational modes of the \textit{R-3m} phase of Sb$_2$Se$_3$ at 0 GPa. The three acoustic IR-active modes are formed by the irreducible representations of $\Gamma_{\text{acoustic}} = A_{2u} + E_u$ and the remaining 12 optical modes are $\Gamma_{\text{optical}} = 2E_g$ (Raman) + $2A_{1g}$ (Raman) + $2E_u$ (IR) + $2A_{2u}$ (IR).

| Irr.evs. | Frequency (cm$^{-1}$) | Raman Intensity ($10^5$ Å$^4$ amu$^{-1}$) | Intensity ($e^2$ amu$^{-1}$) |
|----------|-----------------------|---------------------------------|-----------------|
| $E_g$    | 53.3                  | 0.02                            | Inactive        |
| $A_{1g}$ | 83.7                  | 0.37                            | Inactive        |
| $E_u$    | 86.6                  | Inactive                        | 3.47            |
| $E_u$    | 131.7                 | Inactive                        | 0.03            |
| $E_g$    | 139.4                 | 3.32                            | Inactive        |
| $A_{2u}$ | 145.1                 | Inactive                        | 0.18            |
| $A_{2u}$ | 182.8                 | Inactive                        | 0.29            |
| $A_{1g}$ | 203.8                 | 1.02                            | Inactive        |
this $A_{1g}$ mode is higher than in $\text{Bi}_2\text{Se}_3$ but lower than in $\text{In}_2\text{Se}_3$, as expected from the difference in mass between $\text{In}$, $\text{Sb}$ and $\text{Bi}$. Lower-frequency $E_g$ and $A_{1g}$ modes with much lower intensities are also found around 53 and 84 cm$^{-1}$, respectively, which are again slightly higher than the corresponding frequencies calculated for $\text{Bi}_2\text{Se}_3$. There are four IR-active modes, two with $E_{1u}$ symmetry (87 and 132 cm$^{-1}$) and two with $A_{2u}$ bands (145 and 183 cm$^{-1}$). Of these, the 87 cm$^{-1}$ mode is the most prominent in the spectrum, while the second $E_u$ mode at 132 cm$^{-1}$ is very weak. The two $A_{2u}$ bands have comparable, moderate intensities and form a pair of smaller features at higher frequencies. As expected given the mass difference, the IR-active modes in $\text{Sb}_2\text{Se}_3$ again have slightly higher frequencies than those calculated for $\text{Bi}_2\text{Se}_3$.

### IV. CONCLUSIONS

In summary, we have carried out a comprehensive set of calculations to investigate the stability of five possible phases, viz. $\text{Pnma}$, $R-3m$, $C2/m$, $C2/c$ and disordered $Im-3m$ of the $\text{Sb}_2\text{S}_3$, $\text{Bi}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_3$ sesquichalcogenides under hydrostatic pressures up to 60 GPa.

For the three compounds we find that the monoclinic $C2/m$ and $C2/c$ phases are energetically less favourable throughout the studied pressure range and are not expected to be observed at HP under hydrostatic conditions. On the other hand, the disordered bcc-like $Im-3m$ phase is predicted to be the most energetically stable phase of the three compounds at HP. However, calculated phonon dispersion curves indicate that such a structural phase remains dynamically unstable up to at least 60 GPa for $\text{Sb}_2\text{S}_3$ and $\text{Bi}_2\text{S}_3$. Moreover, the $\text{Pnma}$ phase is stable for the two compounds at HP, even up to 50 GPa; therefore, we do not expect to observe the disordered $Im-3m$ phase in either of these two compounds below 50 GPa. This conclusion agrees with results from Ref. 16, where the disordered phase has not been observed for $\text{Bi}_2\text{S}_3$ up to 65 GPa. However, our results disagree for $\text{Sb}_2\text{S}_3$ with what was reported in Ref. 22, regarding the observation of multiple high-pressure phases. This effect could have been caused by the use of the specific pressure-transmitting medium resulting in non-hydrostatic behaviour during the experimental measurements.

For $\text{Sb}_2\text{Se}_3$ our calculations predict a transition to occur from the $\text{Pnma}$ to the disordered $Im-3m$ phase above 21 GPa. Unlike the former two compounds, at 50 GPa, the $\text{Pnma}$ phase begins to evidence negative phonons at the $\Gamma$-point, thus indicating dynamical instability at HP; whereas the disordered $Im-3m$ phase stabilizes at this pressure range. Our calculations therefore support the conclusion that a phase transition occurs for $\text{Sb}_2\text{Se}_3$ from the $\text{Pnma}$ to the $Im-3m$ phase at HP, in good agreement with experimental findings.

By probing the low-pressure regions, we find that the $\text{Pnma}$ phase is the most stable phase for $\text{Bi}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3$, in good agreement with experiments. However, and unexpectedly, for $\text{Sb}_2\text{Se}_3$, it is the $R-3m$ phase that possess lower energy at 0 GPa, being surpassed by the $\text{Pnma}$ at a moderate pressure range, slightly below 5 GPa and around room-temperature conditions. Since the $\text{Pnma}$ phase is experimentally obtained for $\text{Sb}_2\text{Se}_3$, we suggest that the orthorhombic phase is stabilized by thermal energy at room temperature, which suggests the possibility of synthesizing the $R-3m$ phase under optimized conditions. We would expect the trigonal phase to show topological insulating properties under ambient conditions, which would likely make such an undertaking highly worthwhile. We therefore provide theoretical lattice parameters and atomic positions along with reference IR and Raman spectra to aid future experiments to identify and characterize this phase. We hope that this work will stimulate further investigation of the sesquichalcogenides at high pressure, especially to the lesser-known As analogues of the compounds examined in this work.

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