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First-principles study of the lattice dynamics of Sb$_2$S$_3$

Yun Liu,$^a$ Kun Ting Eddie Chua,$^b$ Tze Chien Sum,$^{c,d,*}$ and Chee Kwan Gan$^{*a}$

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We present a lattice dynamics study of orthorhombic antimony sulphide (Sb$_2$S$_3$) obtained using density-functional calculations in conjunction with the supercell force-constant method. The effect of Born effective charges is taken into account using a mixed-space approach, resulting in the splitting of longitudinal and transverse optical (LO-TO) phonon branches near the zone center. Zone-center frequencies agree well with Raman scattering experiments. Due to the slow decay of the interatomic force constants (IFC), a minimal $2 \times 4 \times 2$ supercell ($Pnma$ setting) with 320 atoms is crucial for an accurate determination of the dispersion relations. Smaller supercells result in artificial acoustic phonon softening and unphysical lifting of degeneracies along high symmetry directions. We propose a scheme to investigate the convergence of the IFC with respect to the supercell sizes. The phonon softening can be attributed to the periodic images that affect the accuracy of the force constants, and the truncation of long-ranged forces. The commensuration of the $\mathbf{q}$-vectors with the supercell size is crucial to preserve degeneracies in Sb$_2$S$_3$ crystals.

1 Introduction

Sb$_2$S$_3$ belongs to the group of metal chalcogenides (A$_2$B$_3$, A=As, Sb, Bi and B=S, Se, Te) that form an important class of semiconductors with extensive applications in photovoltaics$^{1,2}$ and optoelectronics$^3$. They hold great promises as photovoltaic converters and thermoelectric cooling devices$^{4,5}$ due to their small direct bandgaps, high thermoelectric power, and high absorption coefficient in the visible region$^{6,7}$. There is also a surge of interest in using Sb$_2$S$_3$ as a solid-state semiconductor-sensitized solar cell to replace the inorganic dye in dye-sensitized solar cells$^{7,8}$. Sb$_2$S$_3$ has been synthesized to various nanostructured forms, such as nanowires and nanotubes$^{9-11}$, which exhibit enhanced ferroelectric, piezoelectric, and conductive properties.

So far, much focus has been placed on the synthesis and electronic properties$^{12-15}$ of Sb$_2$S$_3$. To complement these known aspects, we present here a study of the lattice vibrational properties of Sb$_2$S$_3$ using density-functional theory (DFT). Phonon dispersion is one of the fundamental properties of crystals and the behavior of the branches reflects specific features of the crystal structure and the interactions between the constituent atoms. These lattice dynamical properties are indispensable in order to understand the properties of interests for device engineering and design, such as electronic transport and lattice specific heat.

We obtain phonon dispersions of Sb$_2$S$_3$ using the supercell force-constant method$^{16-20}$, fully taking into account the effect of Born effective charges. We note that a similar approach has been employed to study Bi$_2$S$_3$ in an earlier work$^{21}$. Due to the slow decay of IFC, we also investigate the effects of supercell sizes on the accuracy of the dispersion relations, and propose a scheme to investigate the convergence of the IFC with respect to the supercell sizes.

2 Methods

The orthorhombic phase of Sb$_2$S$_3$ belongs to the space group $Pnma$ (#62) containing 20 atoms per primitive cell, five of which are inequivalent (Fig. 1). DFT calculations are carried out using the QUANTUM ESPRESSO$^{22}$ suite within the local density approximation (LDA). We use pseudopotentials S.pz-bhs.UPF and Sb.pz-bhs.UPF from http://www.quantum-espresso.org. The electronic wavefunctions are expanded in a plane-wave basis set with kinetic energy cutoff of 75 Ry. The Monkhorst-Pack$^{23}$ $k$-point sampling scheme used for Brillouin zone (BZ) integration has divisions of less than 0.03 Å$^{-1}$. The total energies are tested to converge to within 1 meV/atom.

We relax the atomic coordinates and cell dimensions using a Broyden-Fletcher-Goldfarb-Shanno quasi-Newton algor
scheme to evaluate the matrix elements of the IFC.

The dynamical matrix at a \( \mathbf{q} \) point is obtained by summing the contributions from all atoms in the supercell

\[
D_{st}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{\mathbf{R}} \phi_{st}^{\alpha\beta}(\mathbf{R}) e^{i\mathbf{q}\cdot\mathbf{R}} \quad (2)
\]

where \( s \) and \( t \) run over all atoms in the primitive cell, \( M_s \) is the mass of the \( s \)th atom and \( \mathbf{R} \) is a lattice translation vector. \( \phi_{st}^{\alpha\beta}(\mathbf{R}) \) denotes the IFC between the \( s \)th atom in the primitive cell, and another atom in the supercell that is the image of the \( r \)th atom in the primitive cell under \( \mathbf{R} \). The diagonalization of \( D(\mathbf{q}) \) then yields the phonon frequencies at \( \mathbf{q} \).

2.1 Symmetry Reduction

In order to reduce the number of static DFT calculations, we use the symmetry properties of the crystals to transform the forces\(^{17} \). Only the inequivalent atoms within the primitive cell are displaced to find the forces \( F_{st}^{\alpha} \) between the \( s \)th atom in the primitive cell and \( t \)th atom in the supercell, which can be represented by a \( 3 \times 3 \) matrix. To obtain the forces between an equivalent atom and all other atoms in the supercell, we use the space group operation \( S \) that maps the \( s \)th inequivalent atom to the \( p_s \)th equivalent atom in the primitive cell. The forces between \( p_s \)th and \( p_t \)th atoms can be simply calculated as

\[
F_{p_s p_t} = G(S) F_{st} G(S^{-1}) \quad (3)
\]

where \( G(S) \) represents the point group part of \( S \) in Cartesian coordinates. This approach allows us to displace five atoms in the three spatial directions rather than all 20 atoms in the primitive cell, resulting in substantial saving of the total calculation time.

2.2 Non-analytical correction for \( \mathbf{q} \to 0 \)

Due to the polar character of Sb\(_2\)S\(_3\), the long-range dipole-dipole interaction gives rise to a macroscopic electric field that affects longitudinal optical (LO) phonon modes\(^{28} \). As the transverse optical (TO) modes are not affected, the long range electric fields associated with long-wave longitudinal phonons are responsible for the phenomenon of LO-TO splitting. LO-TO splitting depends on the direction from which one approaches the \( \Gamma \) point in the BZ. This effect is reflected in the non-vanishing Born effective charge tensor \( \mathbf{Z}^* \), taking the form of a non-analytical contribution \( \mathbf{D}_{st}^{\alpha\beta} \) to the dynamical matrix\(^{26,27,29,30} \) in the limit \( \mathbf{q} \to 0 \):

\[
\mathbf{D}_{st}^{\alpha\beta}(\mathbf{q} \to 0) = \frac{4\pi^2}{\Omega} \frac{\sum_{\alpha} Z_{s\alpha}^{\gamma} q_{\gamma} \sum_{\beta} Z_{t\beta}^{\nu} q_{\nu}}{\sqrt{M_s M_t} \sum_{\gamma\nu} \mathbf{e}^{\gamma\nu} \cdot \mathbf{q}}
\]

\[
= \frac{4\pi e^2}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}_{s})_{\alpha} (\mathbf{q} \cdot \mathbf{Z}_{t})_{\beta}}{\mathbf{q} \cdot \mathbf{e}^{\alpha\beta}} \quad (4)
\]

where \( \Omega \) is the volume of the primitive cell, \( e \) is the elementary charge, \( \mathbf{e}^{\alpha\beta} \) is the high-frequency dielectric tensor and \( \mathbf{Z}_{s} \) is the Born effective charge tensor for the \( s \)th atom. \( \mathbf{Z}^* \) and \( \mathbf{e}^{\alpha\beta} \) may be calculated using density-functional perturbation theory (DFPT)\(^{26,27} \).

In order to include the non-analytical correction in the phonon dispersion, we add\(^{31} \) a correction factor \( \tilde{\phi} \) to the real space force-constant \( \phi \):

\[
\tilde{\phi}_{st}^{\alpha\beta}(\mathbf{R}) = \phi_{st}^{\alpha\beta}(\mathbf{R}) + \tilde{\phi}_{st}^{\alpha\beta} \quad (5)
\]
where \( \Phi(R) \) is the corrected real-space inter-atomic force-constant matrix. We may calculate the correction factor \( \tilde{\varphi}_{st}^{\alpha\beta} \) by imposing the condition that

\[
\lim_{q \to 0} \frac{1}{\sqrt{M_i M_j}} \sum_R \varphi_{st}^{\alpha\beta} e^{iq \cdot R} = \tilde{D}_{st}^{\alpha\beta}(q \to 0),
\]

from which we obtain

\[
\tilde{\varphi}_{st}^{\alpha\beta} = \frac{1}{N} \frac{4\pi e^2}{\Omega} \frac{(q \cdot Z_s^\alpha)(q \cdot Z_s^\beta)}{q \cdot \varepsilon^\alpha \cdot q}
\]

where \( N \) is the number of primitive cells in the supercell. The corrected force-constant matrix \( \Phi \) (Eqn. 5) is finally used to calculate the phonon frequencies.

### 3 Results and Discussion

#### 3.1 Born effective charges

Table 2 Non-zero components of the Born effective charge tensor \( Z^* \) and high-frequency dielectric tensor \( \varepsilon^{\alpha\alpha} \) of \( \text{Sb}_2\text{S}_3 \). Components of the five inequivalent atoms are shown for \( Z^* \). The values of the equivalent atoms are the same up to a sign and can be calculated using the transformation relation according to Eqn. 3.

| \( Z^* \) (Sh1) | 2.89 | 5.62 | 7.36 | 0.07 | 1.53 |
| \( Z^* \) (Sb2) | 3.33 | 7.25 | 4.50 | 0.28 | 0.09 |
| \( Z^* \) (S1) | -2.35 | -4.18 | -4.07 | 1.07 | 0.83 |
| \( Z^* \) (S2) | -1.83 | -4.80 | -4.44 | -0.45 | -0.33 |
| \( Z^* \) (S3) | -2.03 | -3.90 | -3.36 | -0.20 | -1.34 |

The Born effective charge \( Z^*_{st}^{\alpha\beta} \), is the first derivative of the macroscopic polarization along the \( \alpha \) direction with respect to the displacement of \( st \) atom along the \( \beta \) direction. This quantity is calculated using linear response theory at the zone center (\( \Gamma \)), and the non-zero values are shown in Table 2. The diagonal elements are different for each \( \text{Sb} \) and \( \text{S} \) atoms, and off-diagonal elements are present, showing considerable anisotropy in the system.

The formal valence charges for \( \text{Sb} \) and \( \text{S} \) are \( +3 \) and \( -2 \), and our calculation shows maximum effective charges of \( +7.36 \) and \( -4.80 \) for \( \text{Sb} \) and \( \text{S} \) respectively. From the study of ferroelectric compounds, it has been suggested that ions with effective charges close to the formal valence charge behave as closed-shell ions. Conversely, the presence of covalent character in the bonds causes a large amount of delocalized charge to flow through the structure during lattice displacements. In \( \text{Sb}_2\text{S}_3 \), the significantly larger effective charges suggest that there is substantial covalent character in the bonds. \( \text{Sb} \) atoms are able to donate electrons to \( \text{S} \) atoms during lattice displacements, and hence increase the magnitude of their respective Born effective charges. These results agree with X-ray photoelectron spectroscopy studies that describe the bonding in \( \text{Sb}_2\text{S}_3 \) as tight covalent.

We also obtain the high-frequency dielectric tensor \( \varepsilon^{\alpha\alpha} \) which is diagonal as shown in Table 2. The anisotropy of \( \varepsilon^{\alpha\alpha} \) is an indication of the anisotropy of \( \text{Sb}_2\text{S}_3 \) structure.

#### 3.2 Zone-center phonons

Since \( Pnma \) is a centrosymmetric space group, the Raman and infra-red (IR) modes of \( \text{Sb}_2\text{S}_3 \) are mutually exclusive, i.e., a mode cannot be simultaneously Raman and IR active. There are 60 phonon modes at \( \Gamma \) that respect the \( D_{2h} \) point group symmetry:

\[
\Gamma = 3 \Gamma_{\text{acoustic}} + 30 \Gamma_{\text{Raman}} + 22 \Gamma_{\text{IR}} + 5 \Gamma_{\text{silent}}
\]

3 are acoustic phonon modes (\( \Gamma_{\text{acoustic}} = B_{1u} + B_{2u} + B_{3u} \)). Of the optical phonon modes, 30 are Raman active (\( \Gamma_{\text{Raman}} = 10A_g + 5B_{1g} + 10B_{2g} + 5B_{3g} \)), 22 are IR active (\( \Gamma_{\text{IR}} = 4B_{1u} + 9B_{2u} + 9B_{3u} \)), and 5 are optically silent (\( \Gamma_{\text{silent}} = 5A_u \)). The \( \text{Sb} \) and \( \text{S} \) atoms have the site symmetry \( C_\infty \) that restrict their motions within the \( xz \) plane for the \( A_g \), \( B_{2g} \), \( B_{1u} \), and \( B_{3u} \) modes, and along the \( y \) axis for the \( B_{1g} \), \( B_{3g} \), \( A_u \), and \( B_{2u} \) modes. This
Table 3 Zone-center phonon modes in Sb$_2$S$_3$ obtained using the supercell force-constant method, DFPT and Raman scattering spectroscopy. Only phonon modes with Raman data are shown. A complete list of Raman active modes are listed in the Supplementary Information.

<table>
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<tr>
<th>Raman mode</th>
<th>Intensity (cm$^{-1}$)</th>
<th>DFPT (cm$^{-1}$)</th>
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<th>Expt. (cm$^{-1}$)</th>
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<td>277.9</td>
<td>278.0</td>
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3.3 Phonon dispersions

Periodic images of displaced atoms can exert sizable effects during the calculation of forces, hence decreasing the accuracy of the IFC. This is not an issue for $q$-vectors that are commensurate with the supercell, since the phonon frequencies calculated at these points are exact using the supercell method. In order to reduce the effects of periodic images on non-commensurate $q$-points, a huge supercell has to be used. However, large primitive cells such as that of Sb$_2$S$_3$ place a computational constraint on the largest supercells that can be used in DFT calculations. As a result, we investigate the effect of supercell sizes on the phonon dispersions by using sizes of $1 \times 4 \times 1$ containing 80 atoms, $2 \times 2 \times 2$ containing 160 atoms and $2 \times 4 \times 2$ containing 320 atoms. We plot the dispersion relations along the high symmetry directions $\Gamma \rightarrow X \rightarrow S \rightarrow R \rightarrow T \rightarrow Z \rightarrow \Gamma$ as shown in Fig. 2, where we have used the $q$-vector convention in Refs. 38,39. Figs. 2(c) shows our most accurate results from the $2 \times 4 \times 2$ supercell calculation.

There are in general 60 phonon modes present in the dispersions, as evident in the $X \rightarrow \Gamma$ and $Z \rightarrow \Gamma$ directions. Double degeneracy occurs along the high symmetry lines $X \rightarrow S$ and $R \rightarrow T \rightarrow Z$, resulting in only 30 distinct phonon frequencies. Along $S \rightarrow R$, the phonon frequencies are quadruply degenerate and only 15 frequencies are present. These degeneracies are preserved in the $2 \times 2 \times 2$ and $2 \times 4 \times 2$ results whereby the zone boundary points $(X,S,R,T,Z)$ are commensurate with the supercell sizes, i.e.,

$$q \cdot L_i = 2\pi n_i$$

where $n_i$ is an integer and $L_i$ are the three supercell lattice vectors. It is interesting to note that commensuration at these points helps to ensure that the entire dispersion along the high symmetry directions also have the correct degeneracies. In contrast, degeneracies are lifted in smaller supercell sizes (Figs 2(a)), as the zone boundary points are not commensurate with the supercell. Commensuration is thus extremely important in low symmetry crystals such as Sb$_2$S$_3$ to preserve the correct degeneracies as opposed to high symmetry crystals which may retain degeneracies even when the commensuration criteria are not met. The conclusion is not specific to Sb$_2$S$_3$ as we also observed the same behaviour for Bi$_2$S$_3$ as shown in the Supplementary Information.

As shown in Fig. 2, the zone-center phonon frequencies of Sb$_2$S$_3$ differ in the $X \rightarrow \Gamma$ and $Z \rightarrow \Gamma$ directions due to macroscopic electric fields in the polar crystals (the so-called LO-TO splitting). $D = (\frac{1}{2}, \frac{1}{2}, 0)$ and $B = (0, \frac{1}{2}, \frac{1}{2})$ are only commensurate with $2 \times 4 \times 2$ supercell, and therefore the agreement between DFPT and supercell results are excellent. There are, however, huge discrepancies in the smaller supercells, showing that the dispersions are not accurate. $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, \frac{3}{8}, \frac{1}{2})$
are not commensurate with any of the supercell sizes, but the results from the supercell force-constant method and DFPT show a good agreement as seen in Figs. 2(c).

Apart from affecting the degeneracies, small supercell sizes also result in the artificial softening of phonon branches, as can be seen in Figs. 2(a) and (b). The softening becomes so severe in the $1 \times 4 \times 1$ supercell that imaginary frequencies are introduced in the acoustic phonon modes. Soft modes are also displayed in the dispersions of $1 \times 1 \times 1$ and $1 \times 2 \times 1$ supercells (see the Supplementary Information).

One of the biggest challenges in phonon calculations is to determine whether the soft modes are artificial (an artefact of the numerical methods, etc) or genuine that are associated with unstable lattice structures and phase transitions. The occurrence of artificial phonon soft modes found in this work should serve as a caution that convergence with respect to supercell size must be checked carefully when using the supercell force-constant method. We conclude that softening is totally absent in the dispersions obtained with a $2 \times 4 \times 2$ supercell for Sb$_2$S$_3$.

The vibrational density of states (vDOS) using the $2 \times 4 \times 2$ supercell result is shown in Fig. 2(d). A dense $10 \times 30 \times 10$ $k$-point mesh is used to sample the BZ and the effect of LO-TO splitting is included.

### 3.4 IFC analysis

We now propose a scheme to analyze the IFC in order to understand the origin of the phonon softening. For each pair of atoms, a $3 \times 3$ force constant matrix is obtained, with elements corresponding to movements of the each atom along the Cartesian directions. As a measure of the strength of this interaction, we use the trace of the IFC tensor, $\text{Tr}(\Phi_{ij})$ which has the advantage of being independent of the coordinate system used.

![Image of phonon dispersions](image_url)

**Fig. 2** (Color online) First-principles phonon dispersions along high symmetry directions for orthorhombic Sb$_2$S$_3$ calculated using the supercell force-constant method for $1 \times 4 \times 1$, $2 \times 2 \times 2$ and $2 \times 4 \times 2$ supercells. The selected $q$-points are $\Gamma = (0, 0, 0)$, $X = (\frac{1}{2}, 0, 0)$, $S = (\frac{1}{4}, \frac{1}{4}, 0)$, $R = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $T = (0, \frac{1}{2}, \frac{1}{2})$, and $Z = (0, 0, \frac{1}{2})$. Blue circles are phonon frequencies calculated from DFPT at $q$-points commensurate with $2 \times 4 \times 2$ supercell, while red circles are frequencies at $q$-points non-commensurate with any of the supercells. Imaginary frequencies (represented by negative frequencies) are present in $1 \times 4 \times 1$ supercell. Degeneracies are preserved in the $2 \times 2 \times 2$ and $2 \times 4 \times 2$ supercells but lost in $1 \times 4 \times 1$ supercell.

![Image of IFC analysis](image_url)

**Fig. 3** (Color online) $\text{Tr}(\Phi_{ij})$ as a function of $r_{ij} = |r_i - r_j|$, the distance between the $i$th and $j$th atom. The $i$th atom is the inequivalent S1 sulphur atom, and $i$ runs through all the atoms within the supercell. The red triangles are data from $1 \times 4 \times 1$ supercell, blue diamonds from $2 \times 2 \times 2$, and black squares for $2 \times 4 \times 2$. The insets show significant interactions beyond the on-site and nearest neighbor atoms.
The decrease of $\text{Tr}(\Phi_{su})$ with increasing interatomic distance $r_{su}$ suggests a suitable range for the interatomic forces.\(^{42}\)

Fig. 3 shows the decay in $\text{Tr}(\Phi_{su})$ as a function of distances for different supercell sizes. The $s$th atom is the inequivalent S1 sulphur atom (Table 1), and $u$ runs through all atoms within the supercell. Although not shown here, similar features are observed when the $s$th atom is replaced by other inequivalent atoms. Although the interactions are dominated by the on-site and the nearest neighbor terms, there are significant non-zero contributions at large distances which show the long ranged interactions in the crystals. The lattice dynamics of Sb\(_2\)S\(_3\) thus cannot be approximated by a simple linear chain model considering only a few nearest neighbor interactions. To correctly describe the dispersions, a large supercell is needed to reduce the effect of periodic images and to capture the interactions at large distances.

Due to the small sizes of $1\times 4\times 1$ and $2\times 2\times 2$ supercells, many values of IFC differ from those of $2\times 4\times 2$ by a few orders of magnitude, as can be seen in Fig. 4. In addition, many interactions beyond $\sim 6$ Å are not captured in the smaller supercells. We believe that these effects destabilize the crystal structure and result the softening of the acoustic phonons. The softening is more pronounced in $1\times 4\times 1$ supercells and less so in $2\times 2\times 2$, due to the larger size of the supercell that reduces the effect of the periodic images and captures more long ranged interactions.

**4 Conclusion**

To the best of our knowledge, the phonon dispersion of Sb\(_2\)S\(_3\) is obtained for the first time through a systematic lattice dynamics study on low symmetry crystals using the supercell force-constant method. The Born effective charges give rise to LO-TO splitting at the zone center and elucidate the covalent character of the bonds. Both the high frequency dielectric tensor and Born effective charges show considerable anisotropy of the crystals. The use of small supercell sizes results in the softening of the phonon modes that is inconsistent with experiments. We attribute this to the effect of the periodic images on the force constants, as well as the truncation of long ranged interactions. We found that a minimal $2\times 4\times 2$ supercell ($Pmna$ setting) is required for an accurate determination of the dispersion relations of Sb\(_2\)S\(_3\). Our results suggest that when using the supercell force-constant method, the supercell size has to be tested with other parameters such as the kinetic energy cut-off, the Brillouin-zone sampling or the self-consistent convergence criteria especially when dealing with low symmetry systems such as Sb\(_2\)S\(_3\).

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