# First-principles study of the lattice dynamics of $Sb_2S_3$

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***Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***
***First published on the web Xth XXXXXXXXXX 200X***
**DOI: 10.1039/b000000x**

## Supplementary Information

Fig. 1 shows the phonon dispersions of $Sb_2S_3$ obtained with smaller $1 \times 1 \times 1$ and $1 \times 2 \times 1$ supercells. Degeneracies are lifted along high symmetry directions. Imaginary frequencies (represented by negative frequencies) are more pronounced in the $1 \times 1 \times 1$ case.

Fig. 2 shows the phonon dispersions of $Bi_2S_3$ obtained using $1 \times 4 \times 1$, $2 \times 2 \times 2$ and $2 \times 4 \times 2$ supercells, as well as the vibrational density of states (vDOS). They exhibit similar features as that of $Sb_2S_3$ [See Section 3.3 of the main text].

Table 1 shows all Raman active phonon modes of $Sb_2S_3$, calculated using the supercell force-constant method and DFPT.

**Table 1** All 30 Raman active phonon modes of $Sb_2S_3$ obtained using the supercell force-constant method and DFPT.

| Raman mode | Intensity $Å^4\ u^{-1}$ | DFPT ($cm^{-1}$) | Supercell ($cm^{-1}$) |
|---|---|---|---|
| $B_{2g}$ | 0.01 | 47.1 | 46.8 |
| $B_{1g}$ | 267 | 47.7 | 47.7 |
| $B_{3g}$ | 1320 | 50.8 | 50.8 |
| $A_g$ | 475 | 54.3 | 54.2 |
| $B_{1g}$ | 2.0 | 68.8 | 68.8 |
| $B_{3g}$ | 1140 | 69.1 | 69.0 |
| $A_g$ | 1160 | 74.5 | 74.2 |
| $B_{2g}$ | 573 | 99.1 | 99.1 |
| $A_g$ | 187 | 100.0 | 100.0 |
| $B_{2g}$ | 228 | 112.4 | 112.1 |
| $B_{2g}$ | 9.3 | 124.1 | 125.0 |
| $A_g$ | 1190 | 131.7 | 131.5 |
| $A_g$ | 2680 | 169.6 | 169.5 |
| $B_{2g}$ | 751 | 171.2 | 171.0 |
| $B_{1g}$ | 3280 | 186.6 | 186.6 |
| $A_g$ | 9970 | 196.7 | 197.4 |
| $B_{3g}$ | 2780 | 198.1 | 198.1 |
| $B_{2g}$ | 130 | 199.7 | 199.5 |
| $B_{3g}$ | 16000 | 200.8 | 200.8 |
| $B_{1g}$ | 1590 | 208.2 | 208.2 |
| $B_{1g}$ | 8990 | 229.3 | 229.3 |
| $B_{3g}$ | 1390 | 231.4 | 231.4 |
| $A_g$ | 4500 | 251.0 | 251.0 |
| $B_{2g}$ | 240 | 254.2 | 254.6 |
| $A_g$ | 56500 | 261.7 | 261.6 |
| $B_{2g}$ | 94.0 | 277.7 | 278.0 |
| $A_g$ | 19100 | 277.9 | 278.0 |
| $B_{2g}$ | 1980 | 286.6 | 285.9 |
| $A_g$ | 4950 | 290.8 | 290.7 |
| $B_{2g}$ | 5090 | 294.3 | 295.9 |

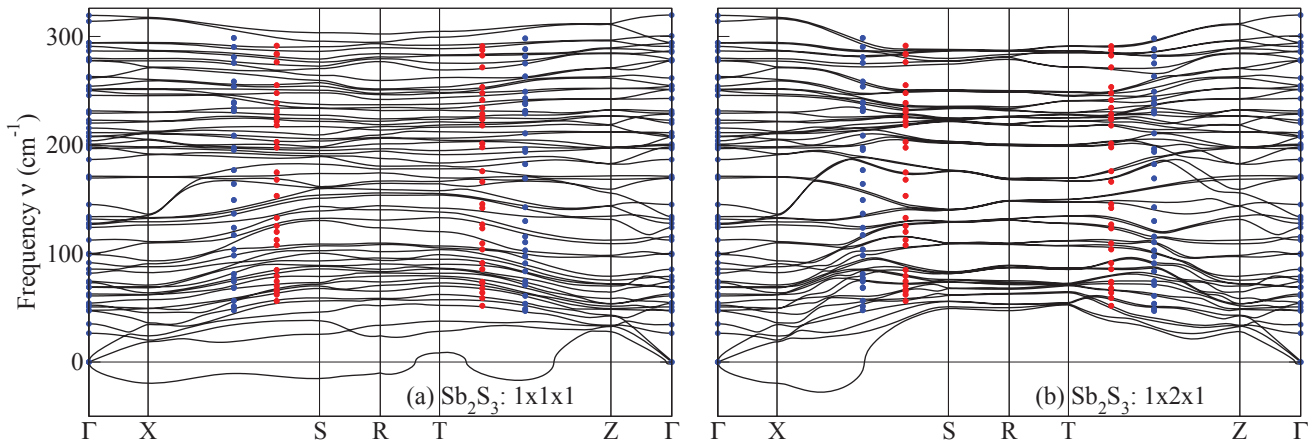


**Fig. 1** (Color online) First-principles phonon dispersions along high symmetry directions for orthorhombic $Sb_2S_3$ calculated using the supercell force-constant method for $1\times1\times1$ and $1\times2\times1$ supercells. The selected **q**-points are $\Gamma=(0,0,0)$, $X=(\frac{1}{2},0,0)$, $S=(\frac{1}{2},\frac{1}{2},0)$, $R=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $T=(0,\frac{1}{2},\frac{1}{2})$, and $Z=(0,0,\frac{1}{2})$. Blue circles are phonon frequencies calculated from DFPT at **q**-points commensurate with $2\times4\times2$ supercell, while red circles are frequencies at **q**-points non-commensurate with any of the supercells.

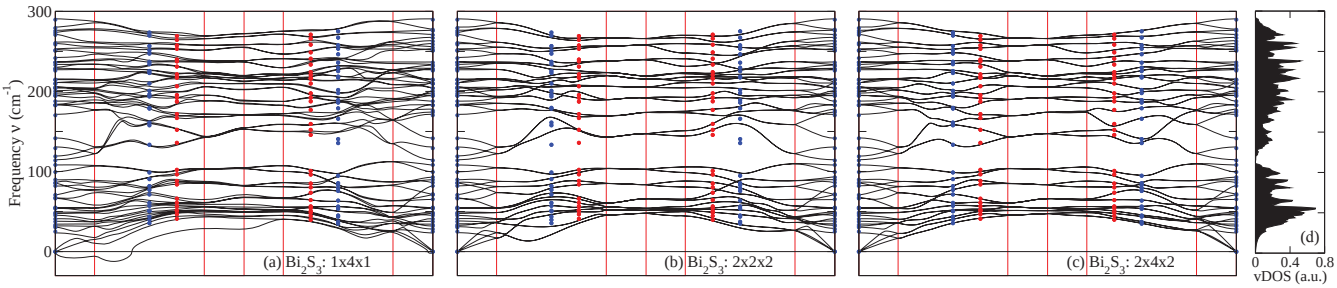


**Fig. 2** (Color online) First-principles phonon dispersions along high symmetry directions for orthorhombic $Bi_2S_3$ calculated using the supercell force-constant method for $1\times4\times1$, $2\times2\times2$ and $2\times4\times2$ supercells. The selected **q**-points are $\Gamma=(0,0,0)$, $X=(\frac{1}{2},0,0)$, $S=(\frac{1}{2},\frac{1}{2},0)$, $R=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $T=(0,\frac{1}{2},\frac{1}{2})$, and $Z=(0,0,\frac{1}{2})$. Blue circles are phonon frequencies calculated from DFPT at **q**-points commensurate with $2\times4\times2$ 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 $1\times4\times1$ supercell. Degeneracies are preserved in the $2\times2\times2$ and $2\times4\times2$ supercells but lost in $1\times4\times1$ supercell.