Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information for: "Identifying Raman Modes of Sb_2Se_3 and their Symmetries using Angle-Resolved Polarised Raman Spectra"

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I. CRYSTAL GROWTH

5N purity Sb_2Se_3 source material (Alfa Aesar) was powdered manually with a mortar and pestle and placed in a quartz ampoule with 4 mm internal diameter. The ampoule was flushed with Ar three times and evacuated to 4×10^{-5} mbar to remove volatile residues. Ar at a pressure of 100 mbar was added to the tube immediately prior to sealing. This was to suppress the parasitic sublimation of Sb_2Se_3 that occurs due to its high vapour pressure [1]. Parasitic sublimation, while not directly detrimental, reduces the proportion of material available for Bridgman melt-growth. The ampoule was placed with the lower tip in line with the temperature peak of the single-zone furnace and heated to 620°C (above the melting point of Sb_2Se_3 at 611°C) then held for around 6 hours to melt and homogenise the powder. The ampoule was then lowered through the natural temperature gradient of the furnace, 0.6°C/mm in the working range, towards the open lower end of the furnace, at a rate of 1.15 mm/hour, rotating at a low speed, the growth process lasting 7 days.

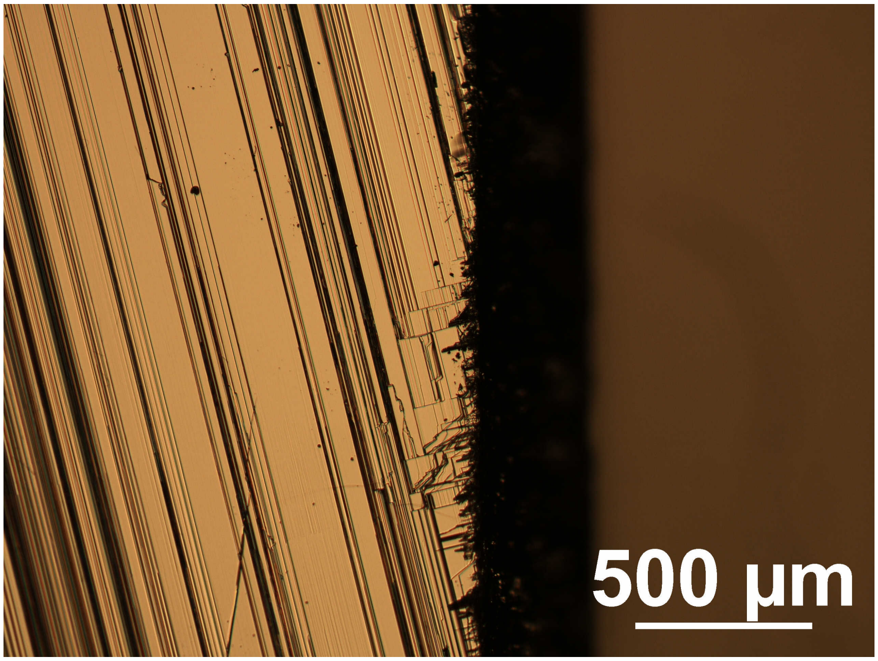

FIG. S1. Parallel lines observed on cleaved surface of bulk crystal using optical microscopy. These were determined to be parallel to the [001] axis of Sb_2Se_3.

TABLE S1. XRD peak positions for the (100), (010) and (001) orientations of Sb_2Se_3 crystals and their FWHM. All values in units of degrees (°).

(100)		(010)		(001)	
2θ	FWHM	2θ	FWHM	2θ	FWHM
15.21	0.040	15.04	0.055	45.56	0.074
30.69	0.046	30.32	0.054	101.52	0.137
46.77	0.065	46.19	0.052		
63.92	0.072	63.06	0.055		
		81.64	0.066		

II. RAMAN THEORY

The Raman scattering intensity (I_s) is given by:

$$I_s = |e_i \mathcal{R}' e_s|^2,$$

where e_i and e_s are the unit polarisation vectors of the incident and scattered light respectively and $\mathcal{R}'$ is the Raman tensor for the mode being studied. The following calculations hold for the analysis of the three crystal planes which are set up perpendicular to the incident beam. The polarisation vectors for the Z(XX)$\overline{\text{Z}}$ case in Cartesian coordinates are as follows:

$$e_i^{\parallel} = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix}, \qquad e_s^{\parallel} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix},$$

while the vectors in the crossed polarisation case, Z(XY)$\overline{\text{Z}}$ become:

$$e_i^{\perp} = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix}, \qquad e_s^{\perp} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The Raman tensors must be expressed in the laboratory frame using the orthogonal transformation matrix, Φ_{xyz} and its inverse $\bar{\Phi}_{xyz}$. The Raman tensor describes the polarisibility of a material and is a tensor quantity. The rotation of the (100) plane of the crystal in the XY-plane in the lab frame is described by:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & cos\theta & sin\theta \\ 0 & -sin\theta & cos\theta \end{pmatrix}^{-1} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & cos\theta & sin\theta \\ 0 & -sin\theta & cos\theta \end{pmatrix}$$

The intensity of a mode is calculated by selecting a suitable e_i, e_s and $\mathcal{R}$. This gives two equations for the Raman intensity of the parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) polarisation configurations for the (100) plane:

$$\begin{aligned} I_s &= |e_i \Phi_{xyz} \mathcal{R} \bar{\Phi}_{xyz} e_s|^2, \\ I_{\parallel}^{XY} &\propto |\alpha_{yy} cos^2\theta + \alpha_{zz} sin^2\theta + \alpha_{yz} sin2\theta|^2, \\ I_{\perp}^{XY} &\propto |\frac{(\alpha_{zz} - \alpha_{yy})}{4} sin2\theta + \alpha_{yz} cos2\theta|^2. \end{aligned}$$

The Raman tensor elements of the D_{2h} point group are as follows [2]:

$$A_g \begin{pmatrix} A & & \\ & B & \\ & & C \end{pmatrix}, \quad B_{1g} \begin{pmatrix} & D & \\ D & & \\ & & \end{pmatrix}, \quad B_{2g} \begin{pmatrix} & & E \\ & & \\ E & & \end{pmatrix}, \quad B_{3g} \begin{pmatrix} & & \\ & & F \\ & F & \end{pmatrix}.$$

The Raman tensor elements were substituted into the two equations for $I_{\parallel}^{XY}$ and $I_{\perp}^{XY}$ above to determine the expected Raman peak intensity variation for each phonon vibrational symmetry. The matrix calculations were repeated for I^{YZ} and I^{XZ}. The results are summarised in the main manuscript in Table 1.

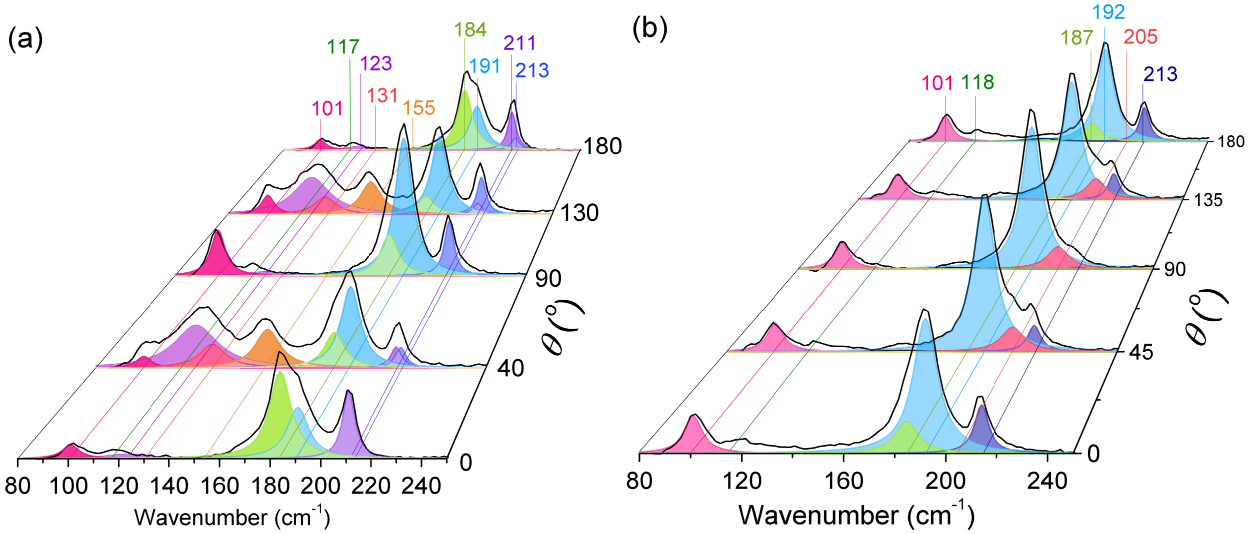

FIG. S2. Selected Raman spectra of Sb_2Se_3 (010) plane (a) and (001) plane (b) rotated through 180° in parallel polariser configuration (solid black lines). Coloured Lorentzian peaks show global fitting results and highlight fitted peak intensity variations.

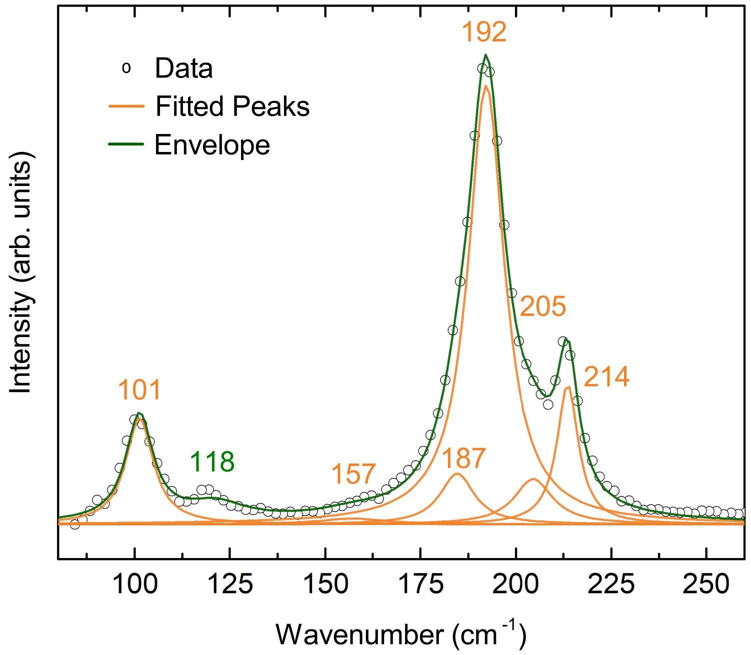

FIG. S3. Fitting of the Raman spectrum of the (001) plane crystal at 20° rotation.

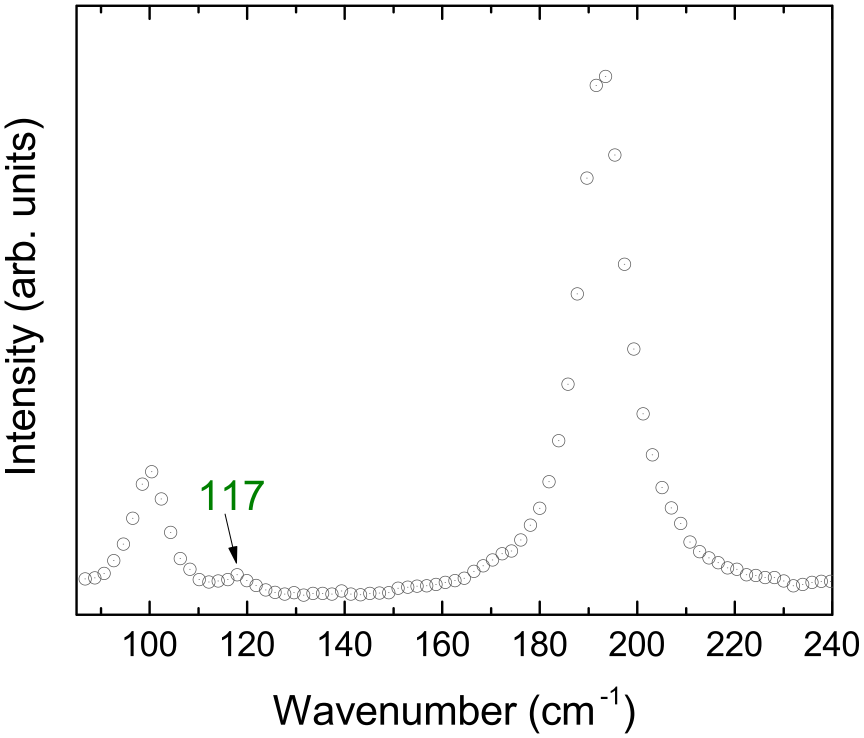

FIG. S4. Raman spectrum of the (100) plane rotated by 90°. The 117 peak is highlighted.

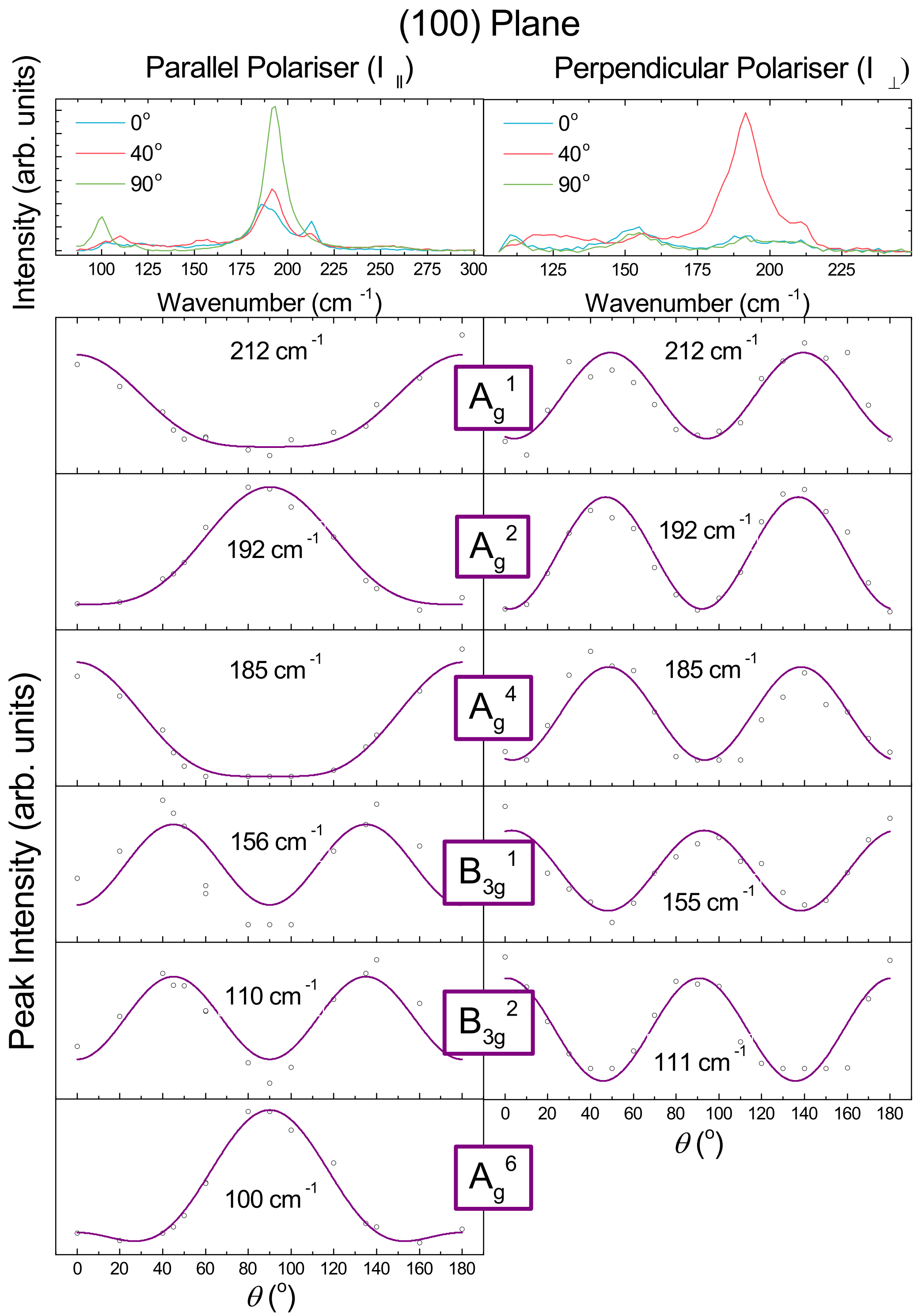

FIG. S5. Representative angle-resolved polarised Raman spectra for Sb_2Se_3 crystal with exposed (100) plane at 0°, 40° and 90° sample rotation (top). Raman peak intensity versus sample rotation of (100) plane peaks (bottom). Circles represent data points and solid lines represent fits to data with dependences described in Table 1 of the main text.

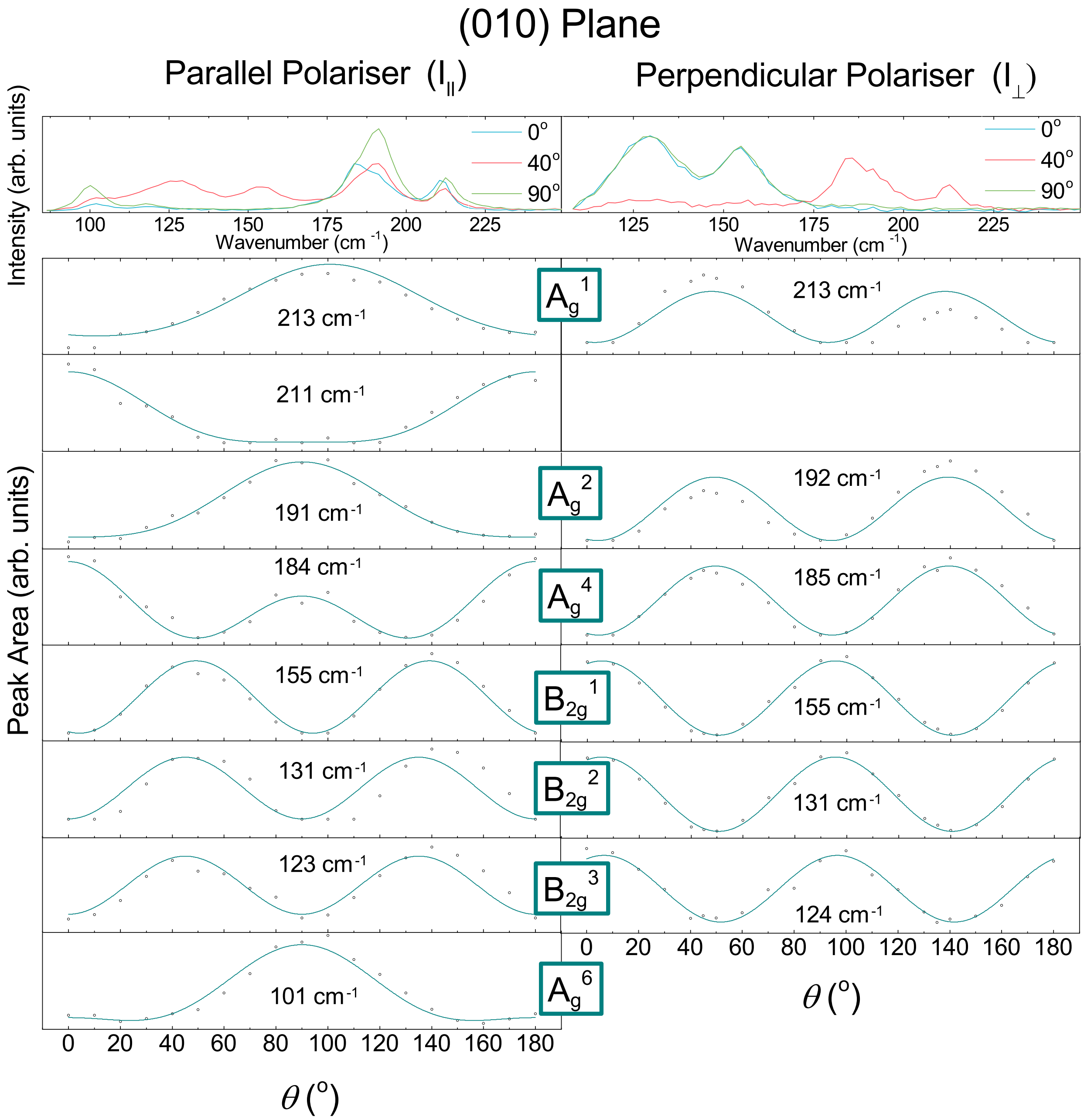

FIG. S6. Representative angle-resolved polarised Raman spectra for Sb_2Se_3 crystal with exposed (010) plane at 0°, 40° and 90° sample rotation (top). Raman peak intensity versus sample rotation of (010) plane peaks (bottom). Circles represent data points and solid lines represent fits to data with dependences described in Table 1 of the main text.

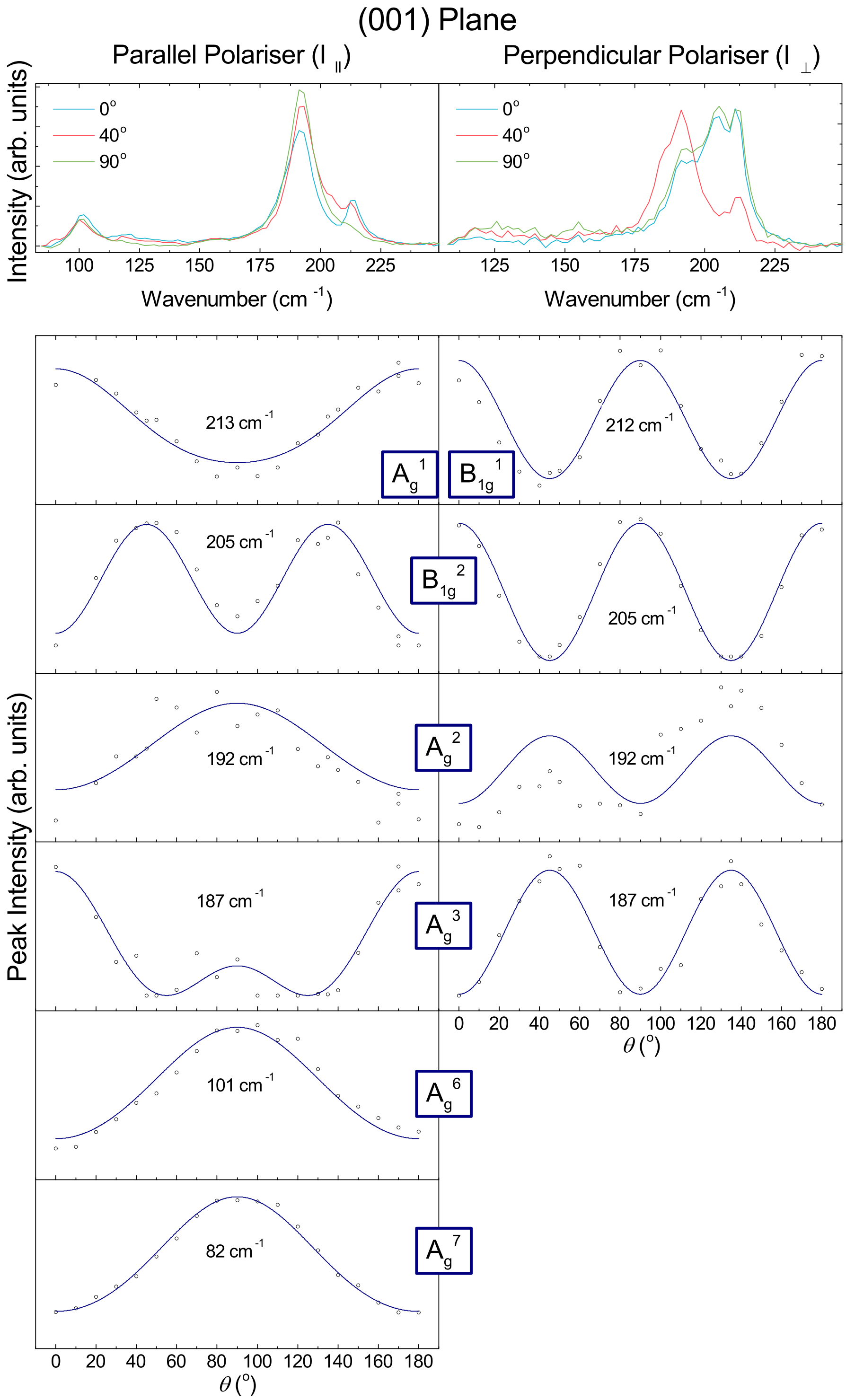

FIG. S7. Representative angle-resolved polarised Raman spectra for Sb_2Se_3 crystal with exposed (001) plane at 0°, 40° and 90° sample rotation (top). Raman peak intensity versus sample rotation of (001) plane peaks (bottom). Circles represent data points and solid lines represent fits to data with dependences described in Table 1 of the main text.

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[1] X. Liu, J. Chen, M. Luo, M. Leng, Z. Xia, Y. Zhou, S. Qin, D. J. Xue, L. Lv, H. Huang, D. Niu and J. Tang, *ACS Applied Materials and Interfaces*, 2014, **6**, 10687–10695.

[2] R. Loudon, *Advances in Physics*, 1964, **13**, 423–482.

[3] P. Vidal-fuentes, M. Guc, X. Alcobe, T. Jawhari, M. Placidi, A. Pérez-Rodríguez, E. Saucedo and V. I. Roca, *2D Materials*, 2019, **6**, 045054.