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## NEUTRON, X-RAY AND LATTICE DYNAMICAL STUDIES OF Sb<sub>2</sub> S<sub>3</sub>

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NEUTRON, X-RAY AND LATTICE DYNAMICAL STUDIES OF  $Sb_2S_3$ K.R. Rao<sup>\*\*</sup>, V.M. Padmanabhan<sup>\*\*\*</sup>, P.R. Vijayaraghavan<sup>\*\*</sup> and S.L. Chaplot<sup>\*\*</sup><sup>\*\*</sup> Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India<sup>\*</sup> Nuclear Physics Division<sup>\*\*</sup> Neutron Physics Division

**Abstract.**- 'Elastic' neutron and x-ray diffraction patterns from crystals of  $Sb_2S_3$  (mineral stibnite) show that the crystals, while ordered along  $\langle 010 \rangle$  (the chain axis), are disordered about  $\langle 010 \rangle$ . Extensive diffuse intensity perpendicular to  $\langle 010 \rangle$  direction is observed. Inelastic scattering studies using 1.4 Å neutrons did not lead to any soft TA modes with  $q$  in the  $(0k0)$  plane and polarised along  $\langle 010 \rangle$ . A few longitudinal phonons along  $\langle 010 \rangle$  are seen. Results from lattice dynamical calculations based on a rigid ion model (with covalent bonding included) are discussed in the context of these observations.

1. **Structure.**-  $Sb_2S_3$  is an interesting photo-conductive ferroelectric semiconductor which crystallises at room temperature in orthorhombic form with spacegroup  $D_{2h}^{16}$  containing four molecules per unit cell. The crystallographic structure shown in Fig.1 consists of ribbons or chains of  $(Sb_4S_6)$  in the b-direction. ( $a = 11.3107 \text{ \AA}$ ,  $b = 3.8363 \text{ \AA}$ ,  $c = 11.2285 \text{ \AA}$ ).

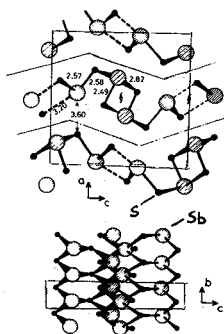


Fig.1 Crystal structure of  $Sb_2S_3$ .

perpendicular to the b-axis. Such intensity patterns are expected of quasi-one-dimensional lattices.

2. **Experimental** - We studied a large natural crystal of mineral stibnite at room temperature (paraelectric) by neutron and x-ray scattering techniques to understand the dynamical properties of the system. Fig.2 is data from 'elastic' neutron diffraction experiments in the  $(h0l)/ (0kl)$  plane (we were unable to distinguish between the a and c axes due to the extensive disorder in the plane). This figure is reminiscent of features observed in case of  $CsD_2PO_4$  by others. The diffraction pattern around  $(040)$  given in Fig.3 clearly shows that the diffraction intensity appears elongated perpendicular to the b-axis.

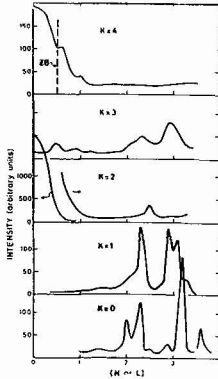


Fig.2 'Elastic' neutron diffraction patterns from  $Sb_2S_3$  in the (h0l)/(0kl) plane.

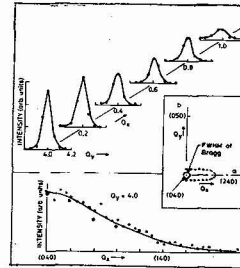


Fig.3 Details of the diffraction intensity around (040).

Fig.4 shows the rotation and Weissenberg x-ray patterns from fibres from the same specimen corroborating neutron results namely, that one observes disorder about  $\langle 010 \rangle$  axis showing extended diffuse streaks; additional diffuse lines are also observed.

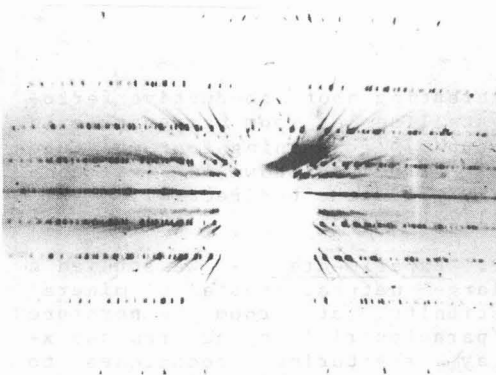


Fig.4 Rotation x-ray photograph of  $Sb_2S_3$ . Rotation about b-axis

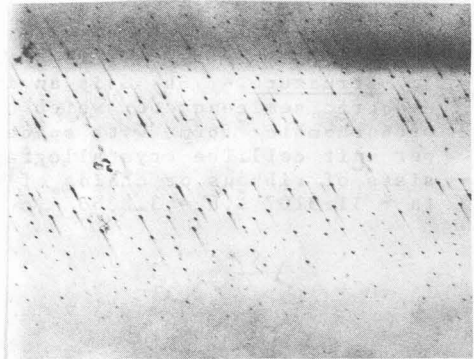


Fig.5 Weissenberg photograph of zero layer of b-axis.

Inelastic neutron scattering experiments permitted us to measure only a longitude branch along  $\langle 010 \rangle$  direction. Experiments to look for TA modes along  $\langle 100 \rangle / \langle 001 \rangle$  direction with polarisation along  $\langle 010 \rangle$  were unsuccessful due to presence of extensive diffuse scattering and poor resolution of the experimental set-up. Fig.6 shows the neutron groups associated with the longitudinal (010) modes.

3. Lattice Dynamical Results - We have carried out lattice dynamical calculations based on a rigid ion model with charges and radii of ions as parameters of the model. Covalent bonding between Sb-S pairs (limited to a distance of 2.6Å) are included. Results of calculations along three high symmetry directions are given in Fig.7.

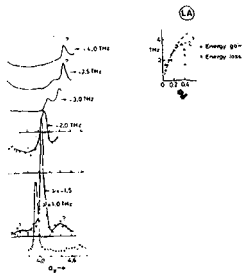


Fig.6 Longitudinal lattice modes as observed by inelastic neutron scattering experiments.

The parameters of the model were chosen so as to provide reasonable cohesive energy and lattice frequencies which cover the infrared and Raman spectral ranges. We observe that there is an extremely soft TA-TO branch in the  $\langle 100 \rangle$  direction; a similar branch may also be noted along  $\langle 001 \rangle$  direction. These branches could give rise to diffuse scattering in neutron and x-ray diffraction patterns. Since these modes are of very low frequency ( $< 0.5$  THz), it is difficult to observe these phonons because of poor resolution. The displacement of atoms at  $q = 0$  for TO mode represents out-of-phase motions of the two chains (each of  $\text{Sb}_4\text{S}_6$  configuration) in the unit cell against each other. Note this can represent interlayer modes if the crystal is thought of as layer-like system.

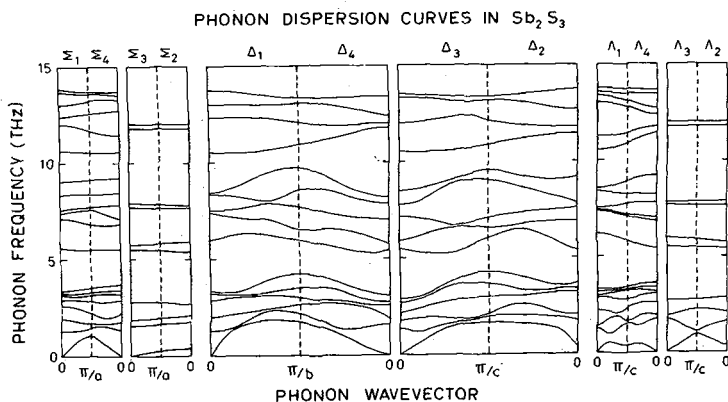


Fig. 7 Calculated phonon dispersion relation in  $\text{Sb}_2\text{S}_3$ .

Details of the experimental observations, dynamical interpretation of calculated results, comparison with data in  $\text{SbSI}$  etc. are to published elsewhere.