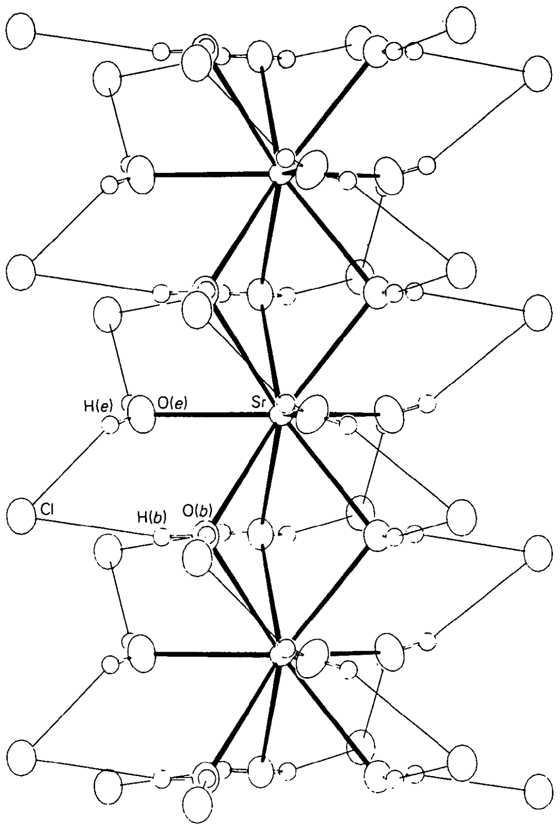

Fig. 1. Part of the $SrCl_2.6H_2O$ structure showing the atomic nomenclature and hydrogen bonding (indicated by thin lines).

is hydrogen-bonded to both an equatorial O [Cl···O(*e*) 3·205 (4), Cl···H(*e*) 2·47 (4) Å] and a bridging O [Cl···O(*b*′) 3·213 (4), Cl···H(*b*′) 2·44 (4) Å] in such a way that triple helices of [···H(*e*)–O(*e*)–H(*e*)···Cl···H(*b*)–O(*b*)–H(*b*)···Cl···] chains of hydrogen bonds spiral round the ···Sr···Sr··· columns. Each $Cl^-$ ion takes part in three of these bonding systems, thus forming six hydrogen bonds.

Careful inspection of the final difference electron density map indicated no residual density >0·27 e $\text{Å}^{-3}$ in a region which would correspond to the alternative hydrogen position. As the peak for H(*e*) appeared in a difference map with a height of 0·85 e $\text{Å}^{-3}$, we conclude that the disorder proposed by Adams & Trumble (1974) is not present.

We thank Dr D. Adams for suggesting the problem, Dr G. Gafner, NPRL, CSIR, Pretoria, South Africa, for the data collection and the Universities of Cape Town and South Africa for support.

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# Structure Determination of Diantimony Tritin Hexasulphide, $Sn_3Sb_2S_6$, by High-Resolution Transmission Electron Microscopy

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**Abstract.** $M_r = 792{\cdot}0$, orthorhombic, *Pnma*, $a = 23{\cdot}18$ (1), $b = 3{\cdot}965$ (1), $c = 34{\cdot}94$ (1) Å, $V = 3211$ $\text{Å}^3$, $Z = 12$, $D_x = 4{\cdot}91$ Mg $m^{-3}$, Cu $K\alpha_1$, $\lambda = 1{\cdot}54056$ Å, $\mu = 107{\cdot}2$ $mm^{-1}$, $F(000) = 4176$, $T = 295$ (3) K. The structure was determined by means of high-resolution transmission electron microscopy. $Sn_3Sb_2S_6$ has a block structure, consisting of lozenge-shaped units of TlI (*B*33) type structure related by glide reflection symmetry.

**Introduction.** High-resolution transmission electron microscopy (HRTEM) permits the direct imaging of crystal structures at resolutions down to approximately 2·5 Å (Iijima, 1971, 1975; Horiuchi, Matsui & Bando, 1976; Bursill & Wilson, 1977). Although such resolution is in general not quite sufficient to resolve individual atoms in projected crystal structures, HRTEM has been used to determine structures that are based on simpler building units whose structure can be inferred from the

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image. Notable examples are the intermediate phases of the $Nb_2O_5$–$WO_3$ system, with structures based on intergrowths of the $ReO_3$ and tetragonal tungsten bronze types (Iijima & Allpress, 1974; Iijima, 1978) and the silicates of the biopyribole group which have ordered structures built from silicate chains of differing widths (Veblen & Buseck, 1979). I report here the structure determination by HRTEM of the ternary sulphide $Sn_3Sb_2S_6$. The structure consists of lozenge-shaped blocks of the TlI structure type, in two orientations related by glide reflection.

A phase of 3:1 composition in the system SnS–$Sb_2S_3$ was first identified by Gaudin & Hamlyn (1938). In a more detailed study, Wang & Eppelsheimer (1976) found that this phase has a solubility range extending from $Sn_3Sb_2S_6$ (3:1) to approximately $Sn_2Sb_2S_5$ (2:1) above 773 K, but that at lower temperatures the range is restricted close to the 3:1 composition. The latter authors showed by X-ray diffraction that the phase crystallizes in the orthorhombic system with space group $Pn2_1a$ or $Pnma$ and lattice parameters $a = 23{\cdot}13$, $b = 3{\cdot}96$, $c = 35{\cdot}01$ Å; from a measured specific gravity of 4·85 the unit-cell contents were determined as $12(Sn_3Sb_2S_6)$, or $M_{60}S_{72}$, where $M$ denotes a metal atom.

**Experimental.** SnS and $Sb_2S_3$ in the ratio 3:1 were melted together in an evacuated silica ampoule at 1123 K for 4 h then annealed at 763 K for 3 d. An X-ray powder diffraction pattern was obtained with a Guinier camera and Cu $K\alpha_1$ radiation with silicon as internal standard ($a = 5{\cdot}4305$ Å); relative peak intensities on the Guinier pattern were measured with a Joyce–Loebl scanning microdensitometer. The powder pattern (Table 1)* is consistent with the unit-cell and space-group data given by Wang & Eppelsheimer (1976); least-squares refinement based on 35 reflections in the range $2\theta = 23{\cdot}3$–$58{\cdot}6°$ gave unit-cell parameters.

For interpretable structural information to be obtained from HRTEM images the structure must be imaged along the short **b** crystallographic axis; unfortunately the crystals cleave parallel to **b** so cleavage fragments could not be used for [010] imaging. Instead, a thin (~20 μm) section cut from the sample was thinned to perforation by ion-beam bombardment and suitably oriented crystals were selected for microscopy. Specimens were examined with a JEOL JEM-200CX electron microscope equipped with a high-resolution objective-lens pole piece ($C_s = 1{\cdot}2$ mm) and a double-tilt goniometer stage (±10°), operating at an accelerating voltage of 200 kV. Exposure times were typically 8 s at a magnification of 550 000 times. Images were recorded at approximately the Scherzer defocus condition [$\Delta f = -1{\cdot}2(C_s\lambda)^{1/2} = -660$ Å] to give optimum contrast (Scherzer, 1949). Figs. 1 and 2 show the [010] electron diffraction pattern and the corresponding image obtained from $Sn_3Sb_2S_6$.

**Discussion.** The high-resolution micrograph shows that in [010] projection the structure of $Sn_3Sb_2S_6$ consists of lozenge-shaped blocks of some relatively simple structure. These blocks are in two orientations which, given

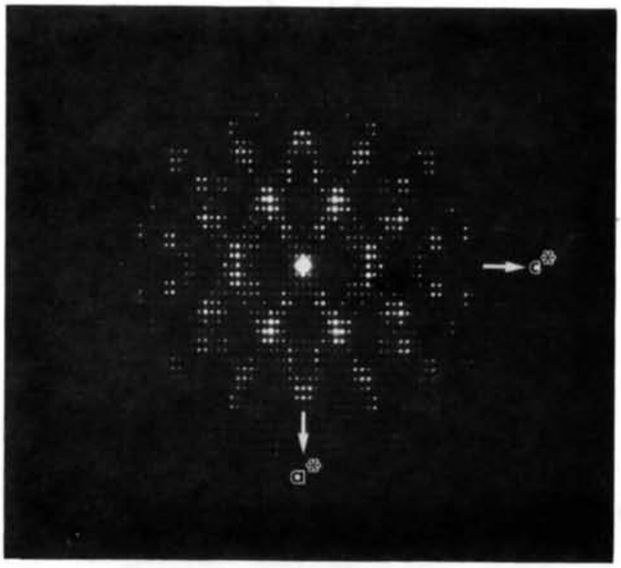

Fig. 1. [010] electron diffraction pattern of $Sn_3Sb_2S_6$.

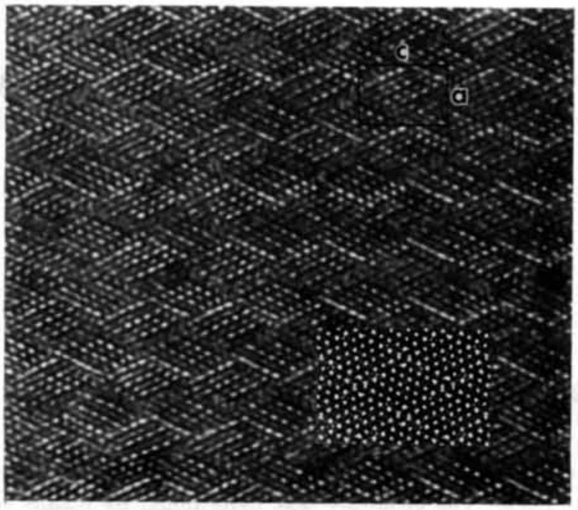

Fig. 2. HRTEM image of $Sn_3Sb_2S_6$ in the [010] orientation. The unit cell is outlined. The inset is a simulated image computed for the structure shown in Fig. 4, assuming a crystal thickness of 100 Å and a defocus of −700 Å.

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* This table, together with other diffraction data, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39098 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the space group $Pn2_1a$ or $Pnma$, must be related by glide reflection symmetry (Fig. 3). Within each lozenge an orthorhombic subcell can be identified, with dimensions 4·0 by 5·6 Å, making an angle of 26° with the *c* axis. The presence of these structural subunits is also evident from the strong substructure reflections in the electron diffraction pattern, but their shape and relative disposition can only be determined from the image. Determination of the structure now reduces to finding the structure of the subunit and the way in which the two non-equivalent types of lozenge surface are matched together.

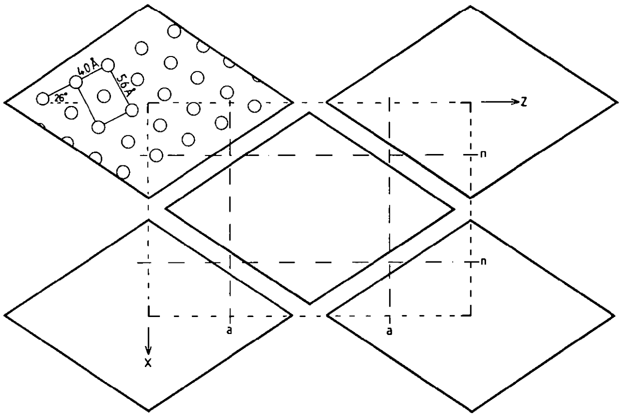

Fig. 3. Schematic diagram of the structure of $Sn_3Sb_2S_6$ showing the *n*- and *a*-glide reflection planes that relate adjacent blocks.

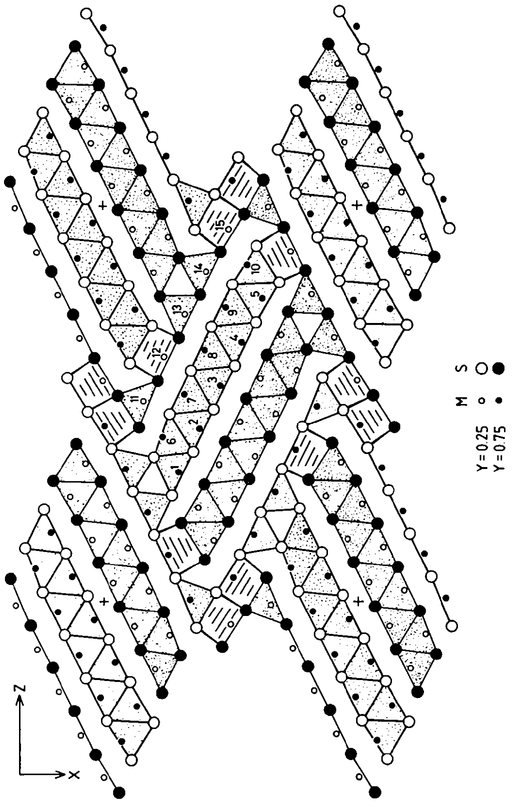

Fig. 4. Proposed crystal structure for $Sn_3Sb_2S_6$ projected on (010).

Table 2. *Positional parameters* ($\times 10^3$) *for* $Sn_3Sb_2S_6$

| | *x* | *y* | *z* |
|---|---|---|---|
| *M*(1) | 295 | 750 | 328 |
| *M*(2) | 378 | 750 | 437 |
| *M*(3) | 461 | 750 | 546 |
| *M*(4) | 543 | 750 | 654 |
| *M*(5) | 626 | 750 | 763 |
| *M*(6) | 235 | 750 | 418 |
| *M*(7) | 318 | 750 | 526 |
| *M*(8) | 400 | 750 | 634 |
| *M*(9) | 483 | 750 | 742 |
| *M*(10) | 565 | 750 | 850 |
| *M*(11) | 157 | 250 | 509 |
| *M*(12) | 240 | 250 | 618 |
| *M*(13) | 323 | 250 | 726 |
| *M*(14) | 407 | 250 | 835 |
| *M*(15) | 496 | 250 | 938 |
| S(1) | 269 | 250 | 270 |
| S(2) | 352 | 250 | 379 |
| S(3) | 435 | 250 | 487 |
| S(4) | 518 | 250 | 596 |
| S(5) | 601 | 250 | 704 |
| S(6) | 693 | 250 | 805 |
| S(7) | 199 | 250 | 366 |
| S(8) | 262 | 250 | 475 |
| S(9) | 345 | 250 | 584 |
| S(10) | 427 | 250 | 692 |
| S(11) | 510 | 250 | 801 |
| S(12) | 605 | 250 | 897 |
| S(13) | 142 | 750 | 442 |
| S(14) | 216 | 750 | 559 |
| S(15) | 299 | 750 | 668 |
| S(16) | 381 | 750 | 776 |
| S(17) | 464 | 750 | 884 |
| S(18) | 557 | 750 | 976 |

Assuming that the structure has the more probable (Nowacki, Matsumoto & Edenharter, 1967) centrosymmetric space group $Pnma$, then the short *b* repeat requires that all atoms be situated on the mirror planes in order to avoid unreasonably close contacts along the *b* axis. The atoms are therefore located at the special position 4(*c*) of $Pnma$, at $\pm(x, \frac{1}{4}, z)$ and $\pm(\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z)$.

The structure of SnS (a distorted variant of the NaCl structure) was adopted for the substructure in a preliminary model. This failed to give a reasonable match at the boundary between adjacent blocks and the required $M_{60}S_{72}$ stoichiometry could not be attained. A slight distortion of the SnS structure leads to the TlI structure (*Strukturbericht* symbol *B*33) which occurs as a structural motif in $Sn_2Sb_2S_5$ (Smith & Hyde, 1983) and in $Sn_4Sb_6S_{13}$ (Jumas, Olivier-Fourcade, Philippot & Maurin, 1980) and is therefore a plausible building unit in $Sn_3Sb_2S_6$. Two possible structures can be derived in this way depending on the sense of the 26° rotation relative to the crystallographic axes of the TlI subunit. Only one of these two alternatives gives a reasonable fit between adjacent blocks; this structure is shown in Fig. 4 and its atomic coordinates are given in Table 2.

The resulting match between adjacent blocks is remarkably simple, thus supporting the initial choice of space group. In the proposed structure only one cation and four anions have been displaced (by <0·6 Å) from their ideal positions to improve the fit. Within the blocks the metal atoms *M*(1)–*M*(10) are each coordinated by seven sulphur atoms forming a monocapped trigonal prism, with the prism axes parallel to **b**. The five metal atoms that lie in the boundary between blocks have the same coordination polyhedron as $M(1)$–$M(10)$, but in the case of $M(12)$ and $M(15)$ the prism axis lies parallel to the mirror plane. Because of the similar atomic scattering factors for Sn and Sb no attempt has been made to assign these species to particular $M$ sites.

Confirmation of the structure presented above for $Sn_3Sb_2S_6$ comes from two lines of evidence. Firstly, the powder X-ray diffraction pattern computed for the model agrees well with that obtained experimentally (Table 1). The $2\theta$ range covered by the data in Table 1 includes 556 allowed reflections; of these only 39 have $(I/I_o)_{\rm calc} > 10\%$ and all such reflections were observed. Secondly, a calculated HRTEM image gives a good match with the experimental image (inset, Fig. 2). The simulated image was computed by the Cowley–Moodie multislice method (Cowley & Moodie, 1957; Goodman & Moodie, 1974). For 1001 diffracted beams and 50 slices (each 2 Å thick) the multislice program uses 25 min of CPU time on a Univac 1100/82 computer; this clearly places a restriction on the use of image calculation as a means of refining structures having a large unit cell.

The structure determination described in this paper provides a good example of the use of HRTEM in a case where, owing to the size of the unit cell and the difficulty of growing good crystals, single-crystal X-ray data may be difficult to obtain and to interpret. The atom positions derived in this study are considered to be correct to within approximately 0·5 Å; a neutron powder diffraction refinement will be attempted at a later date.

The recognition of $Sn_3Sb_2S_6$ as a block structure based on a simpler substructure suggests that its range of composition may result from disorder in the dimensions of the block; further work is in progress to investigate this possibility.

The image computation program was written and developed by P. L. Fejes, A. J. Skarnulis and M. A. O'Keefe. X-ray powder diffraction patterns were calculated by means of the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977), kindly provided by E. Parthé.

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# Neutron Diffraction Refinement of Magnesium Sulfite Hexahydrate, $MgSO_3.6H_2O$

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**Abstract.** $M_r = 212{\cdot}5$, rhombohedral, $R3$, $a = 5{\cdot}933\,(2)$ Å, $\alpha = 96{\cdot}28\,(2)°$, $V = 204{\cdot}8\,(2)$ Å$^3$, $Z = 1$, $D_x = 1{\cdot}72$ g cm$^{-3}$, $\lambda = 1{\cdot}21$ Å, $\mu$(estimated) = $2{\cdot}0$ cm$^{-1}$, $T = 293$ K, $R = 0{\cdot}036$ for 1049 observed neutron reflections. The structure was solved previously from X-ray data but the hydrogen atoms were not located [Flack (1973). *Acta Cryst.* B**29**, 656–658]. The refined dimensions of the $SO_3^{2-}$ ion are S—O = 1·528 (2) Å and O—S—O = 104·3 (1)°. The O—H distances in the water molecules are in the range 0·957 (4)–0·980 (3) Å.

**Introduction.** To evaluate the structure and properties of the lone pair of electrons on S in $SO_3^{2-}$ SCF calculations have been carried out (Strömberg, Gropen, Wahlgren & Lindqvist, 1983). The series

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