The Crystal Structure of γ-In$_2$S$_3$ Stabilized by As or Sb

BY ROLAND DIEHL,* CLAUS-DIETER CARPENTIER AND RUDOLF NITSCHE

Kristallographisches Institut der Universität, D-78 Freiburg/Brsg., Hebelstr. 25, Germany (BRD)

Under normal pressure indium sesquisulphide, In$_2$S$_3$, has a trigonal crystal structure between 754°C and its melting point at around 1090°C. This modification, proposed to be termed γ-In$_2$S$_3$, cannot be quenched to room temperature. Substitution of about 5 at.% of In by As or Sb stabilizes the structure at room temperature. The lattice constants of γ-In$_2$S$_3$(As) are $a = 3.806$ (1), $c = 9.044$ (3) Å, $V = 113.45$ Å^3, $c/a = 2.376$, those of γ-In$_2$S$_3$(Sb) $a = 3.831$ (1), $c = 9.049$ (6) Å, $V = 115.01$ Å^3, $c/a = 2.362$; space group $P\bar{3}m1$, $Z = 1$. X-ray intensity data have been collected on a four-circle automatic single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation. The crystal structure has been solved from a Patterson $h0l$ projection and refined from 532 independent reflexions to $R = 0.056$ for γ-In$_2$S$_3$(As) and 518 independent reflexions to $R = 0.057$ for γ-In$_2$S$_3$(Sb). The S atoms are in a cubic close-packed arrangement with all In atoms in octahedral interstices. Slabs of S–In–S–In–S are stacked along the c axis causing perfect cleavability parallel to (0001). The stabilizing atoms are tetrahedrally coordinated by S within S double-layers of adjacent slabs.

Introduction

Indium sesquisulphide, In$_2$S$_3$, is so far known to occur in three normal pressure modifications. Above 420°C it has a defect spinel structure (Hahn & Klingler, 1949; Rooymans, 1959), which is generally termed α-In$_2$S$_3$. To make the analogy with the spinel formula AB$_2$X$_4$ more evident, α-In$_2$S$_3$ should be better formulated as $\square_{0.33}$In(1)$_{0.66}$In(2)$_2$S$_4$, which is the structural representation of a defect spinel.

It follows from a formulation like this that the sublattice of the tetrahedrally coordinated A atoms is incomplete. It is two thirds occupied by In(1) in random distribution, one third being empty as is indicated by $\square$. With $Z = 8$ one obtains $\frac{8}{3}$ unoccupied tetrahedral interstices per unit cell.

When cooling down α-In$_2$S$_3$ to below 420°C a tetragonal superstructure of the defect spinel is formed (usually termed β-In$_2$S$_3$) with three spinel blocks in the tetragonal **c** direction (Rooymans, 1959; King, 1962; Steigman, Sutherland & Goodyear, 1965). Reduction of this triple unit cell to a body-centred one with half the volume yields [3 . ($\frac{8}{3}$)]/2 = 4 tetrahedral voids ($\square$) which order into a 4_1 screw.

From high-temperature Guinier photographs taken with a Nonius–Lenné camera from room temperature up to the melting point of In$_2$S$_3$ at about 1090°C we found a second phase transformation at 754°C. This transformation had earlier been observed by Hatwell, Offergeld, Herinckx & van Cakenberghe (1961) by means of DTA and by van Landuyt, Hatwell & Amelinckx (1968) when studying single crystals of β-In$_2$S$_3$ with an electron microscope. The latter suggested the

high-temperature modification to be characterized by a random distribution of octahedrally coordinated In(2) atoms. Quenching of this modification to room temperature cannot be achieved.

When investigating phase equilibria in the system indium–arsenic–sulphur with chemical transport reactions, we found a new phase with composition In$_{1.93}$As$_{0.07}$S$_3$ (Diehl, Nitsche & Ottemann, 1970) which revealed a powder pattern practically identical with that of 'pure' In$_2$S$_3$ taken above 754°C. In the system In–Sb–S this phase could also be detected. Thus, it became evident that the second high-temperature modification of In$_2$S$_3$, which we propose to term γ-In$_2$S$_3$, can be stabilized at room temperature by small amounts of As or Sb. To indicate the stabilizing agent we shall further write γ-In$_2$S$_3$(As) and γ-In$_2$S$_3$(Sb). Their crystal data, including the powder patterns, are summarized in an earlier publication (Diehl, Carpentier & Nitsche, 1973).

In order to study the 'structural life' of the compound from room temperature to its melting point the determination of the crystal structure of γ-In$_2$S$_3$ appeared worth while. A complete knowledge of its crystal chemistry could make In$_2$S$_3$ an interesting model substance for a better understanding of the lattice dynamics of structural transformations.

Experimental

Closed-tube iodine transport of In$_2$S$_3$ in an atmosphere of As$_2$S$_3$ or Sb$_2$S$_3$ yielded red plate-like single crystals of γ-In$_2$S$_3$(As) and black ones of γ-In$_2$S$_3$(Sb) (Diehl & Nitsche, 1973, 1975). For X-ray intensity data collection small single crystals in the form of flattened octahedra with well developed faces and a maximum size of about 200 μm were selected and mounted on an Enraf–Nonius CAD-4 four-circle automatic single-

---

* Present address: Institut für Angewandte Festkörperphysik der Fraunhofergesellschaft, D-78 Freiburg/Brsg., Eckerstr. 4, Germany.

crystal diffractometer with κ-geometry. 532 independent reflexions up to $(\sin \theta)/\lambda = 1\cdot3$ Å^{-1} for γ-In$_2$S$_3$(As) and 518 up to $1\cdot1$ Å^{-1} for γ-In$_2$S$_3$(Sb) were measured with a scintillation counter (NaI:Tl) using Zr-filtered, monochromatized Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). Long-time drift of the intensity of the primary beam was corrected by measuring the intensities of the standard reflexions 102 and 110 after every 20 measurements. The background-corrected intensities were further corrected for Lorentz and polarization factors.

The linear absorption coefficients μ for Mo $K\alpha$ radiation are $116\cdot0$ cm^{-1} for γ-In$_2$S$_3$(As) and $117\cdot3$ cm^{-1} for γ-In$_2$S$_3$(Sb). Therefore, absorption correction was performed using the program *ORABS* of the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970). Intensity standard deviations were obtained from counting statistics. 96 reflexions for γ-In$_2$S$_3$(As) and 78 for γ-In$_2$S$_3$(Sb) had an integrated intensity less than three times their standard deviation and were omitted as 'less-thans' from the structure refinement.

Determination and refinement of the crystal structure

Densities were determined with a pycnometer to be $4\cdot75$ (8) g cm^{-3} for γ-In$_2$S$_3$(As) and $4\cdot80$ (8) g cm^{-3} for γ-In$_2$S$_3$(Sb), resulting in one formula unit per unit cell. From Weissenberg and precession photographs possible space groups were found to be $P\bar{3}m1$, $P3m1$ or $P321$. Even after a one-week exposure no evidence of a superstructure could be detected on the photographs. From chemical analyses (Diehl *et al.*, 1973) it was concluded that, on the average, every tenth unit cell contains one stabilizing atom. From packing considerations as well as from the absence of a piezo effect the most probable space group of γ-In$_2$S$_3$ appears to be $P\bar{3}m1$. It was deduced from the lattice constants that the S atoms form close-packed layers, three of which are stacked along the c axis in a cubic close-packed arrangement. The existence of S double layers was indicated by the perfect cleavability observed parallel to (0001). During the early stage of the structure determination the scattering power of the As and Sb was neglected.

A model of the crystal structure of γ-In$_2$S$_3$ was derived from the interpretation of a Patterson synthesis calculated with all $h0l$ reflexions measured for γ-In$_2$S$_3$(As). It is characterized by a cubic close-packed S sublattice with two independent S atoms, one (S$_I$) at position $1(a)$ $(0,0,0)$ the other (S$_{II}$) on $2(d)$ $(\frac{1}{3},\frac{2}{3},z; \frac{2}{3},\frac{1}{3},\bar{z})$ of space group $P\bar{3}m1$ (D^6_{3d}) (No. 164 of *International Tables for X-ray Crystallography*, 1965). The In atoms are located on $2(d)$ in octahedral interstices of the S arrangement. Positional z parameters of S$_{II}$ and In were approximately determined to be $0\cdot313$ and $0\cdot813$, which were the starting parameters for the structure refinement.

The atomic scattering factors for In^{3+} and S^{2-} were taken from Cromer & Waber (1965). $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion in the neutral atoms (Cromer & Liberman, 1970) were applied. A full-matrix least-squares refinement was performed using the program *CRYLSQ* of the X-RAY 70 System (Stewart *et al.*, 1970). With individual isotropic temperature coefficients an R value (defined as $\sum ||F_o| - |F_c||/\sum|F_o|$) of $0\cdot147$ was obtained. Subsequently, a three-dimensional difference Fourier synthesis was calculated. It was fairly featureless except for an outstanding peak at $\frac{2}{3},\frac{1}{3},0\cdot398$ (and, centrosymmetrically related, at $\frac{1}{3},\frac{2}{3},0\cdot602$) which is practically the position of the centre of a tetrahedral interstice of the S packing. Attributing this peak to the scattering power of As^{3+}, a new *CRYLSQ* run was performed (atomic scattering factors and $\Delta f',\Delta f''$ values for As from the same sources as above). Population parameters (PP) for In^{3+} and As^{3+} were allowed to be refined. Using individual isotropic temperature factors an R value of $0\cdot10$ was obtained. Refinement with anisotropic temperature coefficients and an isotropic extinction correction using Larson's (1967) method resulted in an extinction factor of $0\cdot5 \times 10^{-3}$, an absolute scale factor of $5\cdot445$, an R of $0\cdot056$ with 'less-thans' omitted, and $R = 0\cdot068$ with 'less-thans' included. Different weighting schemes were applied to the observed structure factors. Best agreement between the sets of observed and calculated structure factors was obtained using unit weights. After the final refinement cycle the shifts of all positional and temperature parameters were less than 1% of the corresponding standard deviations. The difference Fourier map calculated with all reflexions was featureless.

The same procedure was applied to γ-In$_2$S$_3$(Sb), resulting in an extinction factor of $4\cdot5 \times 10^{-3}$, an absolute scale factor of $7\cdot894$, an R of $0\cdot057$ with 'less-thans' omitted, and $R = 0\cdot066$ with 'less-thans' included.

The F_o, F_c listings for γ-In$_2$S$_3$(As) and γ-In$_2$S$_3$(Sb) are given in Tables 1 and 2.

Results and discussion

The final atomic coordinates are listed in Table 3, the anisotropic temperature coefficients in Table 4. Interatomic distances and angles were calculated by means of the program *BONDLA* of the X-RAY 70 System (Stewart *et al.*, 1970). The results are compiled in Table 5.

The crystal structure of γ-In$_2$S$_3$ is best described as a layer structure. It is similar to that of the A-modification of some rare-earth sesquioxides, *e.g.* A-La$_2$O$_3$ (Pauling, 1929). The layer sequence is illustrated in Fig. 1. The perfect cleavability observed is evident from every third S double-layer being cation-free. In contrast to the cubic close-packed S layers the In layers are in hexagonal close packing. The In atoms are exclusively octahedrally coordinated by S. The concentration of negative charge represented by the empty S double layers causes the In atoms to be appreciably off-centre in the S octahedra.

Table 1. *Observed and calculated structure factors for γ-In$_2$S$_3$(As)*

An asterisk indicates a 'less-than'.

γ-In$_2$S$_3$(As)

Table 2. *Observed and calculated structure factors for γ-In$_2$S$_3$(Sb)*

An asterisk indicates a 'less-than'.

γ-In$_2$S$_3$(Sb)

Table 3. *Atomic positional parameters*

	Position	x	y	z	PP
γ-In$_2$S$_3$(As)					
S$_I$	1(a)	0	0	0	1·0
S$_{II}$	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0·3316 (4)	1·0
In	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0·8097 (1)	0·86 (2)
As	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0·6117 (8)	0·130 (7)
γ-In$_2$S$_3$(Sb)					
S$_I$	1(a)	0	0	0	1·0
S$_{II}$	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0·3331 (4)	1·0
In	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0·8077 (1)	0·94 (2)
Sb	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0·6147 (11)	0·056 (5)

Table 4. *Anisotropic temperature coefficients* ($\times 10^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
γ-In$_2$S$_3$(As)						
S$_I$	5·15 (28)	U_{11}	1·85 (19)	0·5U_{11}	0	0
S$_{II}$	2·45 (11)	U_{11}	2·31 (15)	0·5U_{11}	0	0
In	1·72 (3)	U_{11}	2·44 (5)	0·5U_{11}	0	0
As	1·04 (20)	U_{11}	0·97 (27)	0·5U_{11}	0	0
γ-In$_2$S$_3$(Sb)						
S$_I$	6·56 (39)	U_{11}	1·37 (18)	0·5U_{11}	0	0
S$_{II}$	1·91 (10)	U_{11}	1·98 (13)	0·5U_{11}	0	0
In	1·52 (3)	U_{11}	2·21 (4)	0·5U_{11}	0	0
Sb	1·08 (28)	U_{11}	1·05 (36)	0·5U_{11}	0	0

Table 5. *Interatomic distances* (Å) *and angles* (°)

γ-In$_2$S$_3$(As)		γ-In$_2$S$_3$(Sb)	
S$_I$–S$_{II}$	3·717 (3)	S$_I$–S$_{II}$	3·739 (3)
InS$_6$ octahedron		InS$_6$ octahedron	
In–S$_I$	2·791 (1)	In–S$_I$	2·814 (1)
In–S$_{II}$	2·542 (2)	In–S$_{II}$	2·553 (2)
S$_I$–In–S$_I$	85·97 (3)	S$_I$–In–S$_I$	85·78 (4)
S$_I$–In–S$_{II}$	88·25 (5)	S$_I$–In–S$_{II}$	88·17 (5)
S$_{II}$–In–S$_{II}$	96·97 (7)	S$_{II}$–In–S$_{II}$	97·26 (7)
AsS$_4$ tetrahedron		SbS$_4$ tetrahedron	
As–S$_{II}$	2·257 (2)	Sb–S$_{II}$	2·262 (2)
As–S$_{II}'$	2·535 (9)	Sb–S$_{II}'$	2·548 (11)
S$_{II}$–As–S$_{II}$	114·99 (15)	S$_{II}$–Sb–S$_{II}$	115·76 (18)
S$_{II}'$–As–S$_{II}$	103·14 (21)	S$_{II}'$–Sb–S$_{II}$	102·05 (28)

Stabilization of the γ-In$_2$S$_3$ arrangement is achieved by incorporating As^{3+} and Sb^{3+} into the structure. There is evidence from the structure refinement that the stabilizers are exclusively found in S tetrahedra in the cation-free S double layer which divides the unit cell of γ-In$_2$S$_3$ into two halves. Charge compensation is achieved by empty In sites in the metal layer below or above. The S coordination around the group V elements (see Table 5) is quite characteristic for As^{3+} and Sb^{3+}, which form the apex of a flat trigonal pyramid, the fourth S atom being at a somewhat larger distance (Jellinek, 1968).

The stabilizing power of As^{3+} and Sb^{3+} in the γ-In$_2$S$_3$ crystal structure is felt to be due to the rather

strong binding force between the group V elements and S. thus 'glueing' together the S–In–S–In–S slabs. In addition, a second stabilizing effect is conceivable. When γ-In$_2$S$_3$ transforms into the defect spinel structure of α-In$_2$S$_3$, In atoms have to migrate in part into tetrahedral voids of the S packing. From the As and Sb population parameters it is calculated that the group V elements occupy just one half of those tetrahedral sites of the defect spinel which are not occupied by In(1), thus blocking the migration of In atoms effectively.

It should be mentioned that from a number of chemical analyses performed with different analytical methods (Diehl et al., 1973) it must be concluded that γ-In$_2$S$_3$(As) as well as γ-In$_2$S$_3$(Sb) have a small phase width. Other ternary compounds in the system In–As–S or In–Sb–S have not been observed (Diehl & Nitsche, 1973).

Comparing the crystal structures of β-, α-, and γ-In$_2$S$_3$ one finds that each has a cubic close-packed arrangement of S atoms. At the phase transition points migration of the metal atoms in a rigid S matrix is initiated. Whereas the $\beta \leftrightarrow \alpha$ phase transformation at 420°C is an order–disorder transition, the $\alpha \leftrightarrow \gamma$ transformation is of the reconstructive type. As was observed on high-temperature powder photographs, the polymorphs of In$_2$S$_3$ transform spontaneously into each other within a small temperature interval, indicating a high degree of mobility of the In atoms. A more detailed review paper on the crystal chemistry of indium sesquisulphide will be presented elsewhere.

Fig. 1. Stacking sequence of the γ-In$_2$S$_3$ crystal structure.

References

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104–109.
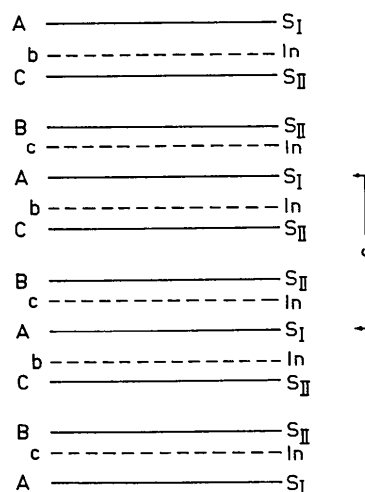DIEHL, R., CARPENTIER, C. D. & NITSCHE, R. (1973). J. Appl. Cryst. 6, 497–498.
DIEHL, R. & NITSCHE, R. (1973). J. Cryst. Growth, 20, 38–46.
DIEHL, R. & NITSCHE, R. (1975). J. Cryst. Growth. 28, 306–310.
DIEHL, R., NITSCHE, R. & OTTEMANN, J. (1970). Naturwissenschaften, 57, 670.
HAHN, H. & KLINGLER, W. (1949). Z. anorg. allgem. Chem. 260, 97–109.
HATWELL, H., OFFERGELD, G., HERINCKX, C. & VAN CAKENBERGHE, J. (1961). C. R. Acad. Sci. Paris, 252, 3586–3588.
International Tables for X-ray Crystallography (1965). Vol. I, 2nd ed., p. 270. Birmingham: Kynoch Press.
JELLINEK, F. (1968). In Inorganic Sulfur Chemistry, edited by NICKLESS. Amsterdam: Elsevier.
KING, G. S. D. (1962). Acta Cryst. 15, 512.
LANDUYT, J. VAN, HATWELL, H. & AMELINCKX, S. (1968). Mater. Res. Bull. 3, 519–528.
LARSON, A. C. (1967). Acta Cryst. 26, 664–666.
PAULING, L. (1929). Z. Kristallogr. 69, 415–420.
ROOYMANS, C. J. M. (1959). J. Inorg. Nucl. Chem. 11, 78.
STEIGMAN, G. A., SUTHERLAND, H. H. & GOODYEAR, J. (1965). Acta Cryst. 19, 967–971.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY 70 System – version of July 1970. Computer Science Center, Univ. of Maryland, College Park, Maryland.