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The Crystal Structure of Tetraindium Triselenide

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The crystal structure of tetraindium triselenide (In_4Se_3) has been determined from three-dimensional X-ray diffractometer data, and refined to a final $R=0{\cdot}06$. The crystals are orthorhombic, space group *Pnnm*, with unit-cell dimensions, $a=15{\cdot}297$, $b=12{\cdot}308$, $c=4{\cdot}081$ Å. $Z=4$. The material is composed of endless interlocking chains running parallel to **c**, consisting of five-membered indium–selenium rings, the chains being cross-linked by strongly bound indium–indium–indium units to form a continuous sheet lying perpendicular to **a**. The structure contains the homonuclear triatomic cation $(In_3)^{5+}$.

Introduction

As part of the continuing investigation of the phases existing in the binary system In–Se (Hogg, 1971), the phase assumed to be In_2Se (Klemm & von Vogel, 1934; Schubert, Dörre & Günzel, 1954; Slavnova & Eliseev, 1963; Slavnova, Luzhnaya & Medvedeva, 1963) has been studied. The crystal structure of In_2Se has been reported (Man & Semilitov, 1965) and is stated to contain the improbably short Se–Se distances of 2·35 Å, much shorter than the Se–Se distances in other indium selenides where they approximate to 4·04 Å, the diameter of the Se^{2-} ion. Since Man & Semilitov state that the intensity data (unpublished) on which their structure is based probably contain large inaccuracies, it was decided to re-investigate the structure. The analysis has established the existence of a phase, In_4Se_3. As this phase has the same cell parameters and space group, and exhibits certain characteristic features of the intensity distribution mentioned by Man & Semilitov for their In_2Se, we conclude that the correct formula for the phase they studied is In_4Se_3.

Experimental

A mixture of indium and selenium powders in correct stoichiometric proportions to produce In_2Se was placed in a sealed evacuated tube held at 700 °C for several hours while being shaken to ensure mixing. The sample was then subjected to directional freezing over a period of three days until it reached 500 °C, at which it was held for a further two days before cooling. The resulting boule was very inhomogeneous, though a few small shiny black needle crystals were extracted which later proved to be In_4Se_3. Preparations using the correct stoichiometric proportions to produce In_4Se_3 again resulted in inhomogeneous boules which also contained the black needle crystals although in somewhat greater quantity.

Unit-cell parameters were obtained using a Siemens four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The unit cell is orthorhombic with $a=15{\cdot}297$ (1), $b=12{\cdot}308$ (1), $c=4{\cdot}081$ (1) Å. These parameters compare well with those given for 'In_2Se' by Man & Semilitov (1965), $a=15{\cdot}24$, $b=12{\cdot}32$, $c=4{\cdot}075$ Å, and by Schubert, Dörre & Günzel (1954) who quoted $a=15{\cdot}26$, $b=12{\cdot}26$, $c=4{\cdot}07$ Å.

The space group, indicated by systematic absences, was either *Pnnm* or *Pnn*2. Solution of the structure and successful refinement gave the space group as *Pnnm* (No. 58), which had apparently been chosen arbitrarily by Man & Semilitov (1965) for 'In_2Se'.

The density was high and proved impossible to measure owing to the exceedingly small quantity of pure phase available, but, assuming the cell to contain $4(In_4Se_3)$, the calculated density is 6·02 g cm^{-3}.

A crystal, with dimensions $230\times69\times35$ μm, was cut from a needle of approximately rectangular cross section, and mounted along the 230 μm direction. Intensities of 754 reflexions, up to a θ value 60°, were measured on the diffractometer with Cu $K\alpha$ radiation; of these 38 were reckoned unobserved (Skapski & Troughton, 1970). The data were corrected for absorption effects according to the method of Busing & Levy (1957) using a grid of $32\times12\times8$, with crystal path lengths determined by the vector analysis procedure of Coppens, Leiserowitz & Rabinovich (1965). The corrected data were found to agree with photographic data obtained with Mo $K\alpha$ radiation and a very small crystal, and measured on a Joyce–Loebl Flying-Spot Densitometer.

The data were corrected for Lorentz and polarization factors and approximate overall scale and temperature factors obtained by Wilson's (1942) method. Reflexions with $h=3n$ were in general stronger than those with $h\neq3n$, thus indicating a degree of pseudo-periodicity along the a axis. This observation was also reported by Man & Semilitov (1965) for 'In_2Se'. In view of this

peculiarity, the space-group agreement, and the very close similarity of the lattice parameters it was initially assumed that the phase obtained was In_2Se. Structure factors calculated using the positional parameters quoted by Man & Semilitov (1965) gave $R=0{\cdot}7$, where $R=\sum(|F_o|-|F_c|)/\sum|F_o|$, but attempts at refinement met with no success. It was concluded that the structure proposed was incorrect.

Determination and refinement of the structure

The *hk*0 projection was solved from sharpened and generalized Patterson projections though difficulty was experienced due to the pseudo-periodicity along the *a* axis, which led to strong **a**/3 vectors in this projection. An asymmetric unit containing eight peaks was derived from the minimum function, but refinement based on these atoms ceased at a relatively high value of *R*. Seven of the atoms proved to be correctly sited, but the eighth, whose *B* factor indicated it did not exist, persistently reappeared on electron-density maps because of the pseudo-periodicity.

After several cycles of block-diagonal least-squares refinement of the *x*, *y* coordinates of the seven atoms using scattering factors which approximate to the mean of those for In and Se, a difference electron-density map enabled the indium and selenium atoms to be identified. The formula was thus established as In_4Se_3.

The *z* parameters were assigned from packing considerations and Patterson sections. Full three-dimensional data were used to refine atomic coordinates and anisotropic thermal parameters by block-diagonal least squares. Twelve reflexions were removed for extinction although these and the 38 reflexions classed as unobserved were included in the computation of the final *R*. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Refinement, carried out in both possible space groups, *Pnnm* and P*nn*2, led to the same final $R=0{\cdot}06$. In *Pnn*2 the final *z* parameters approximated to 0 and $\frac{1}{2}$ to within three standard deviations. It was concluded that the space group was *Pnnm* with all atoms lying on the mirror planes.

The observed and calculated structure factors are listed in Table 1; atomic coordinates and thermal parameters with their standard deviations are quoted in Table 2. The numbering of the atoms in the asymmetric unit and a projection of the structure viewed

Table 1. *Observed and calculated structure factors*

Data in each block are arranged in columns of *h*, F_o and F_c

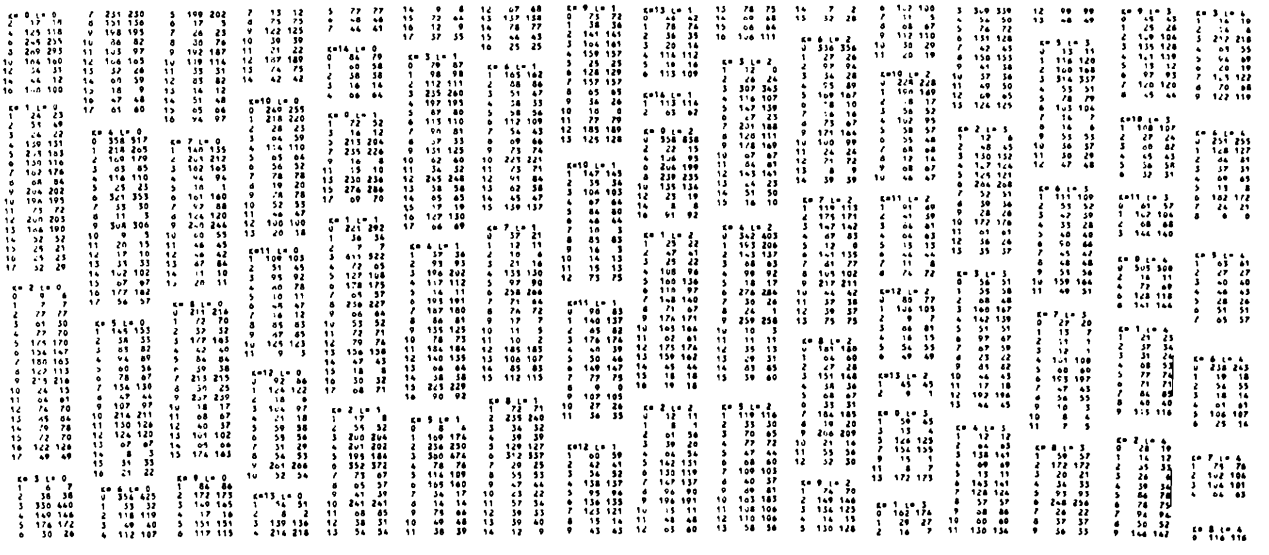

Table 2. *Fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* ($\times 10^4$ Å^2) *with e.s.d.'s in parentheses*

Thermal parameters defined as $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)]$

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	$2U_{12}$
In(1)	7111 (1)	3393 (1)	0	148 (6)	102 (6)	82 (6)	61 (11)
In(2)	8157 (1)	5236 (1)	0	145 (6)	151 (6)	166 (7)	110 (11)
In(3)	9675 (1)	6442 (1)	0	113 (6)	129 (6)	77 (6)	32 (11)
In(4)	4238 (1)	3974 (1)	0	226 (7)	224 (7)	243 (8)	−74 (13)
Se(1)	9033 (1)	8493 (2)	0	160 (9)	139 (9)	108 (10)	−9 (17)
Se(2)	7688 (1)	1386 (2)	0	170 (10)	139 (9)	120 (10)	12 (17)
Se(3)	4239 (1)	1560 (2)	0	133 (9)	177 (10)	106 (10)	−7 (17)

along **c** is shown in Fig. 1; a perspective view of part of the structure is shown in Fig. 2.

Description of the structure

The structure is planar in the **c** direction with all atoms lying in sheets on $z=0,\frac{1}{2}$. Analysis of interatomic distances led to the system of bonding shown in Figs. 1 and 2 and indicated that the material is composed of endless chains of atoms running parallel to **c** based on five membered indium–selenium rings [atoms In(1), Se(2), In(2_1), In(3_1), Se(1_1)]. These chains are cross linked by strong In–In–In bonds [atoms In(1), In(2), In(3)] to form a continuous sheet perpendicular to **a**. The structure contains two such sheets, centrosymmetrically related, which interlock as shown in Fig. 1. One such sheet is shown in Fig. 2. Bond lengths and angles with their standard deviations for atoms within a sheet are given in Table 3. Distances between atoms in neighbouring sheets are given in Table 4 with relevant Se–Se distances.

The distances between Se atoms in the z direction is determined by the c parameter of the unit cell (4·081 Å), which indicates that the selenium atoms exist in the doubly ionized state; the diameter of the Se^{2-} ion is 4·04 Å. In(4) appears rather loosely bound to Se(3), the bond length being 2·97 Å compared with the aver-

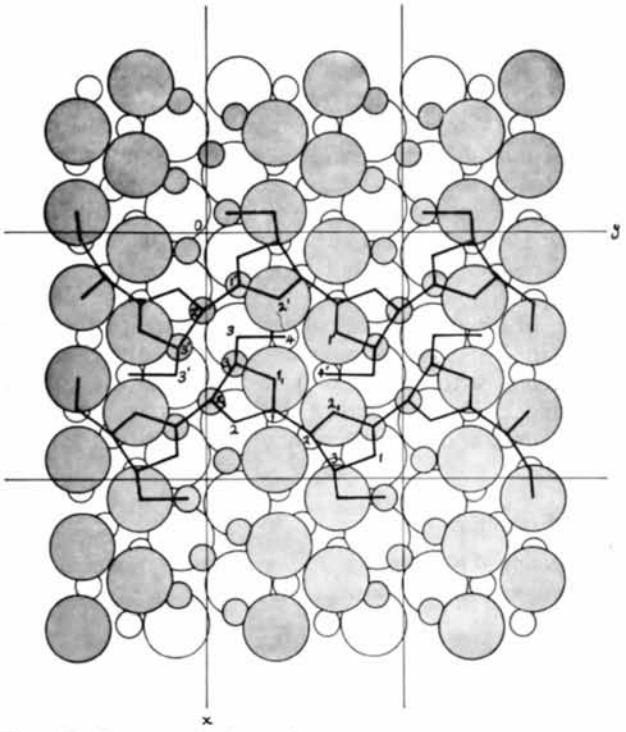

Fig. 1. In_4Se_3. A projection of the structure down **c** showing the method of bonding. The atoms are scaled to the respective ionic radii of In^{3+} (0·81 Å) and Se^{2-} (2·02 Å). Shaded and non-shaded atoms lie on $z=\frac{1}{2}$ and 0 respectively. Atom numbers refer to Tables 2, 3 and 4.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Atomic positions are as shown in Figs. 1 and 2. Subscripts 1 and 2 indicate atoms with $z=+\frac{1}{2}$ and $-\frac{1}{2}$ respectively.

Se(1) –In(3)	2·709 (3)	In(3)—In(2)—In(1)	157·8 (1)
In(3)—In(2)	2·756 (2)	$Se(2_1)$–In(2)—$Se(2_2)$	93·6 (1)
In(2)—In(1)	2·776 (2)	$Se(2_1)$–In(2)—In(3)	96·7 (1)
In(1)—Se(2)	2·623 (3)	$Se(2_1)$–In(2)—In(1)	98·5 (1)
Se(2) –$In(2_1)$	2·800 (2)	In(2)—In(1)—Se(2)	125·1 (1)
$Se(1_1)$–In(1)	2·691 (1)	$Se(1_1)$–In(1)—$Se(1_2)$	98·6 (1)
$In(3_1)$–Se(3)	2·635 (1)	$Se(1_1)$–In(1)—In(2)	109·7 (1)
Se(3) –In(4)	2·971 (3)	$Se(1_1)$–In(1)—Se(2)	105·2 (1)
		In(1)—$Se(1_1)$–$In(3_1)$	101·1 (1)
		$Se(1_1)$–$In(3_1)$–$In(2_1)$	101·3 (1)
		$Se(1_1)$–$In(3_1)$–Se(3)	100·2 (1)
		$In(2_1)$–$In(3_1)$–Se(3)	124·1 (1)
		$In(3_1)$–Se(3) –$In(3_2)$	101·5 (1)
		$In(3_1)$–Se(3) –In(4)	93·2 (1)
		$In(2_1)$–Se(2) –In(1)	108·7 (1)

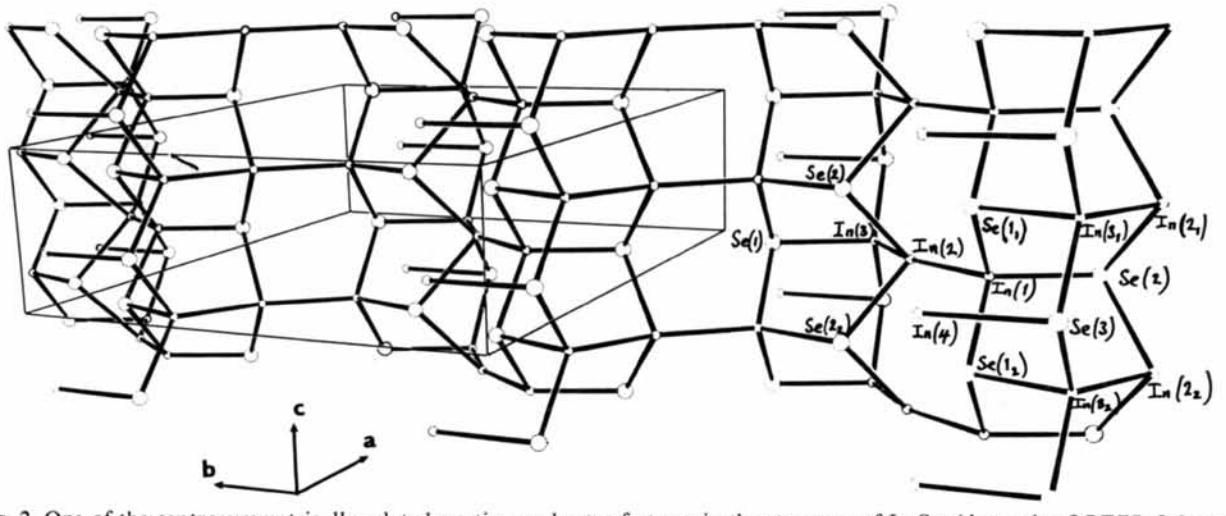

Fig. 2. One of the centrosymmetrically related continous sheets of atoms in the structure of In_4Se_3 (drawn by *ORTEP*, Johnson, 1965). Small circles are In atoms, large circles are Se atoms. The part of the structure shown covers 3 cell translations in the b direction and 2·5 in the **c** direction. Atom designations refer to Tables 2, 3 and 4.

Table 4. *Other relevant interatomic distances* (Å) *with e. s. d.'s in parentheses*

In–Se and In–In distances < 4 Å and Se–Se distances < 4·8 Å are given. Atomic positions are as shown in Figs. 1 and 2.

In(4)—In(4′)	3·437 (2)	Se(2′)–Se(1′)	4·112 (3)
In(4)—Se(1′)	3·739 (2)	$Se(1_1)$–Se(1′)	4·745 (3)
In(4)—$Se(1_1)$	3·393 (2)	$Se(1_1)$–Se(3)	4·100 (3)
In(4)—Se(2′)	3·159 (2)	$Se(1_1)$–Se(2)	4·221 (3)
Se(3) –In(1′)	3·842 (2)	Se(3) –Se(2′)	4·023 (3)
Se(3) –In(2′)	3·434 (2)	Se(3) –Se(3′)	4·491 (3)
$In(3_1)$–In(3′)	3·686 (2)	Se(2) –Se(3′)	4·673 (3)
In(2)—In(4′)	3·791 (2)		

age of 2·69 Å for the other In–Se bonds, thus probably indicating that In(4) is singly ionized. In this connexion it is interesting to note that the thermal parameters of In(4) are almost double those for the other indium atoms. The next-nearest neighbour to In(4) is Se(2′) at 3·16 Å, which suggests a weak bonding between these two atoms which lie in different sheets.

The very short bonds in the In–In–In trio average 2·77 Å, which is much shorter than the elemental indium bond of 3·24–3·36 Å, and indicates the presence of the triatomic cation $(In_3)^{5+}$ (Hogg, Sutherland & Williams, 1971) analogous to the $(Hg_3)^{2+}$ ion proposed by Torsi & Mamantov (1970). In ionic terms the formula of the phase would, therefore, be In^+ $(In_3)^{5+}$ $3(Se)^{2-}$. The structure of the $(In_3)^{5+}$ cation can be envisaged in terms of a digonal hybridization of the central atom. This would lead ideally to a linear arrangement of the three atoms whereas there is a bend of 22·2° at the central atom. This bending can be explained if the selenium atoms are sp^3 hybridized, each being bonded to three indium atoms (Fig. 2) and carrying a lone pair. The bending is due to a repulsion of the central indium atom by the lone pair of the neighbouring Se atom.

The short bonds found in the In–In–In units existing in this structure are paralleled by bonds of 2·74 and 2·76 Å in the structures of In_6S_7 (Hogg & Duffin, 1967) and In_6Se_7 (Hogg, 1971) respectively.

Additional note

Just prior to the submission of this paper we received a copy of a note, by Mme Anna Likforman and M Jean Etienne (Likforman & Etienne, 1972), reporting a duplicate determination of the structure of In_4Se_3. It is based on only 207 reflexions and refined to $R = 0{\cdot}09$. Within limits their results agree fairly well with ours, though a different interpretation is placed on the bonding. In devising our scheme we did not consider contacts greatly in excess of the sum of the covalent radii of the atoms involved and see no justifiable reason for changing our conclusions. The proposal in our preliminary communication of an ionic formula has been construed by these workers to mean that the structure is ionic; this is not so. We feel that their Weissenberg data (the type of radiation is not quoted) are not sufficiently extensive to discriminate between the two possible space groups for this material. Their note also contains several typographical errors, more serious amongst which are the interchange of the columns of x and y coordinates in Table 1 and the incorrect labelling of Se(3) in Fig. 1.

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