

for the heavy atom, whereas the C atoms move with their minimum amplitude perpendicular to the Pd-C direction and the N atoms move along that direction. This inversion may be influenced by the presence of H bonds. In the cation, the motion is described with ac-

curacy but it does not obey definite laws. The N(3) atom motion is the least anisotropic and the least amplified. Amplitudes increase for the atoms at the bottom of an ethyl group.

No attempt to correct bond lengths for thermal motion has succeeded. The approximations of riding motion and of independent vibrations have been used but it may necessitate having to account for an important libration.

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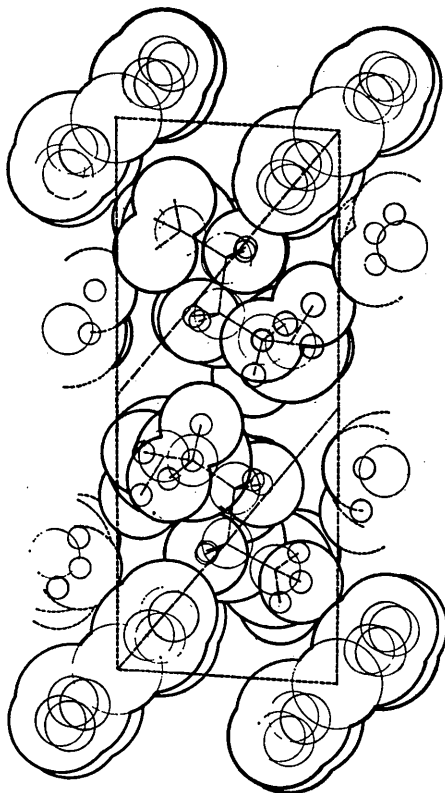


Fig. 7. Section in the structure through the (010) plane.

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The Crystal Structure of In_6Se_7

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The crystal structure of In_6Se_7 has been determined from powder and single-crystal data and is shown to be isomorphous with that of In_6S_7 . The unit cell, which contains two formula units, is monoclinic with $a=9.430$, $b=4.063$, $c=18.378$ Å, $\beta=109.34^\circ$ and the space group is $P2_1$. Basically the structure consists of two separate sections of almost cubic close-packed arrays of Se atoms with In atoms in octahedral coordination, the two sections having equivalent directions at 61° to each other.

Introduction

In their investigations of the phases existing in the In-Se system, Slavnova, Luzhnaya & Medvedeva (1963) and Slavnova & Eliseev (1963) described a black

crystalline phase to which they ascribed the formula In_5Se_6 .

This phase has been examined by the author as part of an X-ray crystallographic examination of the In-Se system. The structural analysis of the phase shows that

its correct chemical formula is In_6Se_7 and that it is, with minor differences, isomorphous with In_6S_7 , whose structure was determined by Hogg & Duffin (1967).

Preparation of the phase

The phase was prepared by heating In_2Se_3 to 1000°C in an argon flow of 0.04 litres/minute. This resulted in the slow loss of the more volatile component, selenium, enabling a very fine control of the stoichiometry of the sample to be maintained by varying the length of the heating period. X-ray powder analysis showed that the required duration to produce In_6Se_7 was about 30 minutes.

Unit cell and space group

Powder data showed that the unit cell of In_6Se_7 was monoclinic with lattice parameters $a = 9.430 \pm 0.005$, $b = 4.063 \pm 0.001$, $c = 18.378 \pm 0.004$ Å, $\beta = 109.34 \pm 0.05^\circ$ which compare closely with those of In_6S_7 determined by Duffin & Hogg (1966). $\text{Cu K}\alpha$ powder data were collected using a Nonius-Guinier focusing powder camera and a Philips diffractometer; in both techniques metallic indium was used as an internal calibration.

Measurements were made on the first 80 lines in the powder patterns, the lattice parameters being fitted by the least-squares method to the photographic data since the Guinier technique gave better resolution of closely spaced reflexions. The diffractometer data were used as a comparison to detect possible systematic errors that arise from different causes in the two techniques, but in fact the very close agreement between the two sets of data showed that these were small. The lattice parameters allow two formula units per unit cell giving a calculated density of 6.21 g.cm^{-3} , compared with $6.10 \pm 0.02 \text{ g.cm}^{-3}$ obtained by the toluene-displacement method.

Systematically absent reflexions, as determined from b -axis single-crystal Weissenberg photographs, were of the type $0k0$ with k odd, indicating the space group $P2_1$ or $P2_1/m$. As with In_6S_7 , the relative intensities of corresponding reflexions on even layer lines were very similar as were the corresponding reflexions on odd layer lines. This strongly implied that all the atoms were on or near planes separated by $\frac{1}{2}$ in y . If the former were the case, as it was with In_6S_7 , the space group would be $P2_1/m$, all the atoms lying on the special positions $2(e)$ and with $y = \frac{1}{4}$ or $\frac{3}{4}$. However, the structural analysis revealed that the atoms are slightly, but significantly, displaced from these planes so that the correct space group is $P2_1$.

Structure determination

Single-crystal intensity data from 1430 independent reflexions were collected from Weissenberg photographs taken about the b axis using $\text{Cu K}\alpha$ radiation and multiple-film exposures. Reflexion intensities were meas-

ured using a Joyce-Loebl flying-spot integrating microdensitometer, except for very weak reflexions which had to be estimated visually. The two sets of data were placed on the same scale by measuring, with the flying-spot microdensitometer, the more intense reflexions of the calibrated scale used for the visual estimation.

Data were corrected for Lorentz and polarization factors and, in the case of the visual data, for spot elongation on upper layer lines. Tables of Bond (1959) were used to correct for absorption, assuming that the crystal was a cylinder of mean radius 0.025 mm, the axis of the cylinder being parallel to b . The crystal was in fact needle-like and roughly elliptical in cross section with maximum and minimum radii 0.029 and 0.020 mm, respectively.

The analysis started with a determination of isotropic temperature and scale factors by means of Wilson plots. Corrected scaled intensity data were then used to compute a Patterson projection onto the (010) plane and this was found to be so similar to that obtained by Duffin & Hogg for In_6S_7 , that it was concluded at this stage that the two structures must be isomorphous or very nearly so. A three-dimensional least-squares refinement of the structure in the space group $P2_1$ was undertaken using as initial atomic coordinates those found for In_6S_7 . The initial R value was 0.26 and this was reduced to 0.114 by several further cycles of refinement, at which stage the shifts in the coordinates were much less than the standard deviations. The final positional coordinates of the atoms together with their standard deviations and isotropic temperature factors are given in Table 1. Table 2 lists the calculated and observed structure factors. Data for each layer line was put onto an absolute scale by means of Wilson plots; final adjustments, which proved small, were made by scaling each layer separately several times during the refinement. Anisotropic temperature terms were not refined in view of the nature of the absorption correction. During refinement the least-squares program moved the atoms off the planes $y = \frac{1}{4}$ and $y = \frac{3}{4}$, which was not the case during the analysis of In_6S_7 . Although the atoms were shifted only slightly from these planes, the displacements were, in general, several times greater than the appropriate standard deviations.

Refinement of the structure in the space group $P2_1/m$ in which the y coordinates of the atoms are fixed at $\frac{1}{4}$ or $\frac{3}{4}$ resulted in a higher final R value of 0.121, but the x , z and thermal parameters were within the standard deviations of those resulting from refinement in $P2_1$.

An electron-density projection along the b axis contained no spurious peaks other than those due to series-termination effects. The corresponding difference Fourier synthesis was virtually featureless except for two small negative regions lying on either side of an In atomic site with two corresponding positive regions oriented at right angles to the negative ones. This effect could be due to (1) the use of isotropic temperature factors (2) an absorption correction being too approximate or (3) the occurrence of extinction. The possi-

Table 1. Atomic parameters with standard deviations

Values of x , y and z are in fractions of the unit cell edges. Standard deviations are shown in parentheses.

	x	y	z	B (\AA^2)
In(1)	0.0569 (3)	0.2564 (14)	0.1241 (1)	2.35 (4)
In(2)	0.3662 (2)	0.2579 (13)	0.1871 (1)	1.83 (3)
In(3)	0.4105 (2)	0.7658 (12)	0.3954 (1)	2.04 (4)
In(4)	0.1363 (2)	0.2474 (14)	0.4662 (1)	2.13 (4)
In(5)	0.2031 (3)	0.7408 (17)	0.7284 (2)	2.97 (5)
In(6)	0.3056 (2)	0.2588 (13)	0.9529 (1)	1.71 (3)
Se(1)	0.1693 (4)	0.7458 (18)	0.0065 (2)	1.71 (5)
Se(2)	0.2190 (4)	0.2414 (19)	0.3410 (2)	2.00 (5)
Se(3)	0.5132 (4)	0.7523 (20)	0.2732 (2)	1.85 (5)
Se(4)	0.4651 (3)	0.7595 (18)	0.9080 (2)	1.49 (5)
Se(5)	0.0651 (4)	0.2538 (20)	0.8204 (2)	1.92 (5)
Se(6)	0.0629 (4)	0.2438 (19)	0.5926 (2)	1.92 (5)
Se(7)	0.3631 (4)	0.7412 (19)	0.5329 (2)	1.80 (5)

Table 2. Observed and calculated structure factors

Data in each block are arranged in columns of L , F_o and F_c . Unobserved reflexions have been allocated on intensity $I_{min}/2$ where I_{min} is the smallest observable intensity.

L	F_o	F_c
000	1000	1000
001	1000	1000
002	1000	1000
003	1000	1000
004	1000	1000
005	1000	1000
006	1000	1000
007	1000	1000
008	1000	1000
009	1000	1000
010	1000	1000
011	1000	1000
012	1000	1000
013	1000	1000
014	1000	1000
015	1000	1000
016	1000	1000
017	1000	1000
018	1000	1000
019	1000	1000
020	1000	1000
021	1000	1000
022	1000	1000
023	1000	1000
024	1000	1000
025	1000	1000
026	1000	1000
027	1000	1000
028	1000	1000
029	1000	1000
030	1000	1000
031	1000	1000
032	1000	1000
033	1000	1000
034	1000	1000
035	1000	1000
036	1000	1000
037	1000	1000
038	1000	1000
039	1000	1000
040	1000	1000
041	1000	1000
042	1000	1000
043	1000	1000
044	1000	1000
045	1000	1000
046	1000	1000
047	1000	1000
048	1000	1000
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075	1000	1000
076	1000	1000
077	1000	1000
078	1000	1000
079	1000	1000
080	1000	1000
081	1000	1000
082	1000	1000
083	1000	1000
084	1000	1000
085	1000	1000
086	1000	1000
087	1000	1000
088	1000	1000
089	1000	1000
090	1000	1000
091	1000	1000
092	1000	1000
093	1000	1000
094	1000	1000
095	1000	1000
096	1000	1000
097	1000	1000
098	1000	1000
099	1000	1000
100	1000	1000

bility of extinction is suggested by the fact that the low-angle intense reflexions have observed structure factors which are, in general, less than the calculated values. This was checked by calculating the function $\beta(2\theta)$ given by Zachariassen (1963). A plot of $\beta(2\theta)$ against 2θ for the affected reflexions approximately followed the theoretical curve, indicating the presence of extinction. A correction for extinction was, not made however, because of the imprecise nature of the absorption correction and because replacing F_o with F_c for the affected reflexions did not, on refinement, shift the atomic coordinates by amounts exceeding the standard deviations, although the R value was reduced to below 0.09. Exclusion of the affected reflexions resulted in shifts to the positional parameters which again did not exceed the standard deviations.

Description of the structure

Interatomic distances up to 4.2 Å and their standard deviations were calculated and are listed in Table 3. The atoms referred to in this Table are given in Fig. 1 which shows the contents of four adjacent unit cells projected onto the (010) plane. The structure, which is very similar to that of In_6S_7 , consists of two separate sections of cubic close-packed arrays of selenium atoms with indium atoms in octahedral coordination. These two sections, whose limits in the c axis direction are shown in Fig. 1, lie across the centre and end section of the unit cell and can be brought into the same orientation by rotating one of them through 61° about the

[010] direction. The two sections are continuous throughout the structure in the direction of the a and b axes but the close packing scheme of the end section is considerably distorted on inversion across the origin of the unit cell. The Se-Se distance in the y direction is given by the b parameter of the unit cell, 4.063 Å, which agrees closely with the value of 4.04 Å for the diameter of the Se^{2-} ion as given by Clark (1955). The Se-Se distances in other directions are of the order of 3.8 to 3.9 Å indicating a general distortion of the structure similar to, but slightly greater than, that occurring in In_6S_7 .

Table 3. *Interatomic distances*

Standard deviations are shown in parentheses. Atoms labelled (a) or (b) lie near the planes $y = -\frac{1}{4}$ and $y = \frac{1}{4}$ respectively.

In(1)—In(2)	2.760 (5)
In(1)—Se(1)	3.355 (6)
In(1)—Se(1a)	3.407 (6)
In(1)—Se(1')	2.630 (6)
In(1)—Se(5')	2.689 (7)
In(1)—Se(5'a)	2.704 (7)
In(2)—Se(2)	3.534 (6)
In(2)—Se(3)	3.647 (6)
In(2)—Se(3a)	2.681 (6)
In(2)—Se(4')	2.725 (6)
In(3)—Se(2)	2.728 (6)
In(3)—Se(2b)	2.607 (6)
In(3)—Se(3)	2.725 (6)
In(3)—Se(7)	2.708 (6)
In(3)—Se(7')	2.996 (6)
In(3)—Se(7'b)	2.857 (6)
In(4)—Se(2)	2.663 (7)
In(4)—Se(6)	2.634 (6)

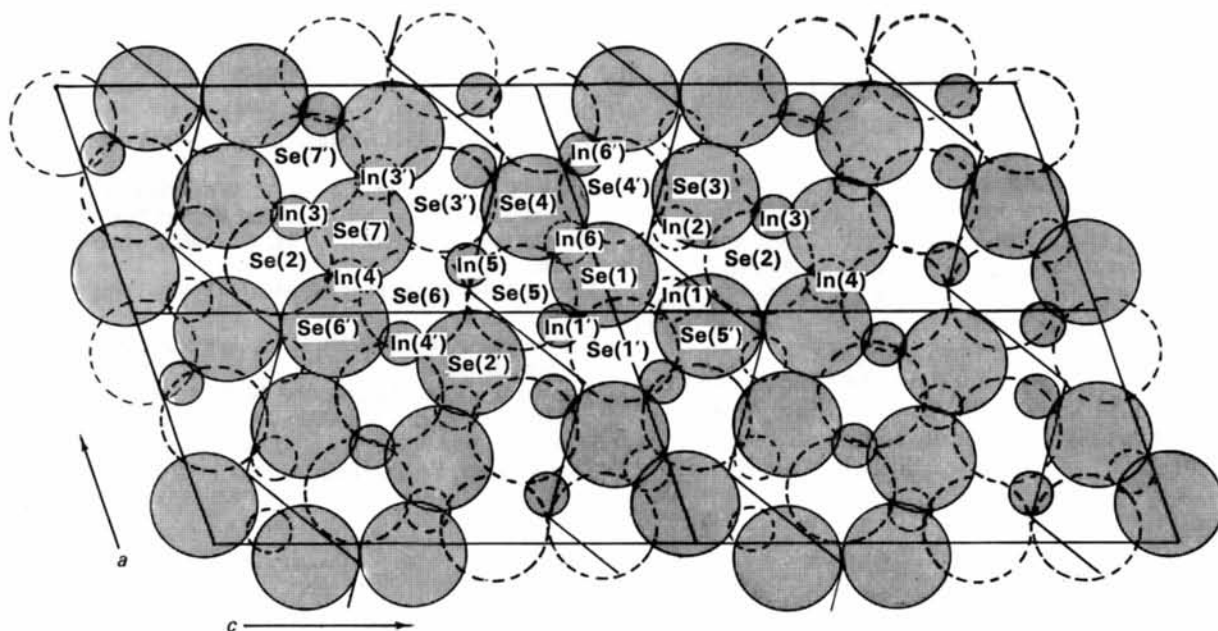


Fig. 1. The structure of In_6Se_7 . The contents of 4 adjacent unit cells with some neighbouring atoms projected onto the (010) face. Atoms lying near the plane $y = \frac{1}{4}$ are shaded and those near $y = -\frac{1}{4}$ are drawn with broken lines. The relative radii of the atoms are those given by Clark (1955) for the In^{3+} and Se^{2-} ions, 0.81 and 2.02 Å respectively. The numbers in parentheses refer to the atomic designations in Tables 1 and 3.

Table 3 (cont.)

In(4)—Se(6')	2.724 (6)
In(4)—Se(6'a)	2.746 (6)
In(4)—Se(7)	2.892 (6)
In(4)—Se(7a)	2.927 (6)
In(5)—Se(3')	3.340 (7)
In(5)—Se(3'b)	3.396 (7)
In(5)—Se(4)	3.406 (7)
In(5)—Se(5)	3.149 (7)
In(5)—Se(5b)	3.216 (7)
In(5)—Se(6)	3.142 (7)
In(5)—Se(6b)	3.157 (7)
In(6)—Se(1)	2.716 (6)
In(6)—Se(1a)	2.794 (6)
In(6)—Se(4)	2.811 (6)
In(6)—Se(4a)	2.808 (6)
In(6)—Se(4')	2.747 (6)
In(6)—Se(5)	2.724 (7)
Se(1)—Se(1')	3.724 (7)
Se(1)—Se(4)	3.796 (7)
Se(1)—Se(4')	3.831 (7)
Se(1)—Se(4'b)	3.889 (7)
Se(1)—Se(5)	3.800 (7)
Se(1)—Se(5b)	3.835 (7)
Se(2)—Se(3)	3.981 (8)
Se(2)—Se(3a)	3.935 (8)
Se(2)—Se(5')	3.879 (8)
Se(2)—Se(5'a)	3.826 (8)
Se(2)—Se(6')	3.856 (8)
Se(2)—Se(6'a)	3.846 (8)
Se(2)—Se(7)	3.902 (7)
Se(2)—Se(7a)	3.903 (7)
Se(2)—Se(7')	3.854 (7)
Se(3')—Se(4)	3.978 (7)
Se(3')—Se(4a)	3.948 (7)
Se(3')—Se(6)	3.942 (8)
Se(3')—Se(7)	3.907 (8)
Se(3')—Se(7a)	3.953 (8)
Se(4)—Se(4')	3.811 (7)
Se(4)—Se(5)	4.125 (7)
Se(4)—Se(5b)	4.102 (7)
Se(6)—Se(6')	3.800 (8)
Se(6)—Se(7)	3.920 (7)
Se(6)—Se(7a)	3.931 (7)
Se(6')—Se(7)	3.914 (7)
Se(7)—Se(7')	3.783 (7)

Average In—Se distances for the three octahedrally coordinated indium atoms In(3), In(4) and In(6) are 2.770, 2.764 and 2.766 Å respectively. These values are smaller than the sum of the ionic (2.84 Å) radii of the elements and the value of 2.95 Å quoted by Semilitov (1961) for an octahedrally coordinated indium atom in the low temperature form of In_2Se_3 .

Indium atoms In(1), In(2) and In(5) lie on the junction of the two sections of close packing. Atom In(1) is approximately tetrahedrally coordinated with Se(5'), Se(5'a), Se(1') and In(2) which itself is approximately

tetrahedrally coordinated with Se(3), Se(3a), Se(4') and In(1). Average In—Se distances in these tetrahedra are smaller than those for the octahedrally coordinated indium atoms, being 2.67 and 2.68 Å for In(1) and In(2) respectively; these compare more closely with the In—Se tetrahedral covalent bond length of 2.58 Å than with the In—Se ionic bond length of 2.84 Å. The In(1)—In(2) distance of 2.760 Å, which is very similar to the value of 2.741 Å for the same bond in In_6S_7 , is the only short In—In distance in the structure and probably indicates an interaction between these two atoms. It is considerably smaller than the indium elemental bond length (3.24 Å) and lies closer to the value of 2.88 Å for the tetrahedral covalent diameter of indium.

Indium atom In(2) is unique in that it is closely coordinated with the selenium atoms Se(3) and Se(4') which belong to the centre and end sections of close packing respectively. Atom In(5) is also unusual since its position in the structure is such that given a small displacement it could belong to either of the two sections. It is therefore loosely bound with an average distance from the nearest selenium atoms of 3.26 Å compared with 2.76 Å for the octahedrally coordinated In(4), thus accounting for the high temperature factor assigned to it by the least-squares program.

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