The Structural Chemistry of Indium Phosphorus Chalcogenides

By Roland Diehl* and Claus-Dieter Carpentier

Kristallographisches Institut der Universität, Hebelstrasse 25, D-7800 Freiburg im Breisgau, Federal Republic of Germany

Indium phosphorus chalcogenides are so far known to occur as $InPS_4$, $In_4(P_2S_6)_3$ and $In_4(P_2Se_6)_3$. Indium thiophosphate, $InPS_4$, is tetragonal, space group $I\bar{4}$ (S_4^2), with $a = 5.623$ (1), $c = 9.058$ (2) Å, $c/a = 1.611$, $V = 286.4$ (1) Å³, and $Z = 2$. Its crystal structure was refined from 753 independent X-ray reflexions measured with an automatic four-circle single-crystal diffractometer to $R = 0.038$. The absolute configuration was obtained by refinement calculations including anomalous-dispersion factors. $In_4(P_2S_6)_3$ is monoclinic, space group $P2_1/c$ (C_{2h}^5), with $a = 6.842$ (2), $b = 10.528$ (2), $c = 18.266$ (5) Å, $\beta = 107.67$ (2)°, $V = 1253.7$ (4) Å³, and $Z = 2$. The crystal structure, refined from 2630 independent X-ray reflexions to an R value of 0.063, was found to be a metal-deficient threefold superstructure of the $Fe_2P_2S_6$ type formed by the ordering of metal vacancies. Similar relationships hold for $In_4(P_2Se_6)_3$ with respect to $Fe_2P_2Se_6$ but the former builds up a sixfold superstructure of the latter. Indium selenohypodiphosphate is orthorhombic, space group $Pba2$ (C_{2v}^8), with $a = 19.197$ (9), $b = 11.090$ (9), $c = 20.067$ (7) Å, $V = 4272.2$ (8) Å³, and $Z = 6$. From analogies with the S compound as well as from geometrical and space-group considerations, its crystal structure was established.

Introduction

The metal (M) phosphorus chalcogenides (Ch = S, Se) can be subdivided into two compound families. The first is represented by the general formula M_xPCh_4 with x values so far known to be 3, 1·5 and 1. The following M thiophosphates have so far been synthesized and structurally characterized: Cu_3PS_4 (Garin & Parthé, 1972) with $x = 3$; $Pd_3(PS_4)_2$ (Bither, Donohue & Young, 1971), $Co_3(PS_4)_2$, $Hg_3(PS_4)_2$, $Sr_3(PS_4)_2$, $W_3(PS_4)_2$ (Sokalov & Nechaeva, 1969) with $x = 1·5$; BPS_4 (Weiss & Schaefer, 1963), $AlPS_4$ (Weiss & Schaefer, 1960), $GaPS_4$ (Buck & Carpentier, 1973), $InPS_4$ (Carpentier, Diehl & Nitsche, 1970), $BiPS_4$ (Zimmermann, Carpentier & Nitsche, 1975), $CrPS_4$ (Diehl & Carpentier, 1976) with $x = 1$. Most of these compounds are characterized by a more or less distorted close-packing of S atoms with M in tetrahedral or octahedral interstices of the packing but with P being exclusively in tetrahedral S coordination. Because of the strong P–S bonding within the PS_4 group, indicated by an average bond length of 2·03 Å, the compounds should be classified as thiophosphates.

Up to now, Cu_3PSe_4 (Garin & Parthé, 1972) and Tl_3PSe_4 (Isaacs, Gottlieb & Feichtner, 1974) are the only known seleno compounds which belong to this formula type. So far, no structural analysis of the latter has been reported.

* Present address: Institut für Angewandte Festkörperphysik der Fraunhofer-Gesellschaft, Eckerstrasse 4, D-7800 Freiburg im Breisgau, Federal Republic of Germany.

The second family of M–P–Ch compounds is structurally characterized by P_2Ch_6 units with a P_2 group in octahedral Ch coordination. These compounds are to be classified as chalcogenohypodiphosphates. Close packing of the chalcogen atoms has been encountered in the crystal structures of compounds $M_2P_2Ch_6$ with M = Mn, Fe, Co, Ni, Zn, Cd, Hg, Mg, Ca, V, Pd in octahedral interstices of the Ch packing (Klingen, Ott & Hahn, 1973). The compounds $Sn_2P_2S(Se)_6$ and $Pb_2P_2S(Se)_2$ (Carpentier, 1974) have complicated crystal structures with no close packing of the Ch atoms.

Besides the divalent metals Pd, Co and Hg, indium was found to be the first trivalent metal to form phosphorus chalcogenides which are encountered in both compound families: Apart from $InPS_4$, the unrefined crystal structure of which we have reported in

Table 1. *Crystal data*

	$InPS_4$	$In_4(P_2S_6)_3$	$In_4(P_2Se_6)_3$
a (Å)	5·623 (1)	6·842 (2)	19·197 (9)
b (Å)	–	10·528 (2)	11·090 (9)
c (Å)	9·058 (2)	18·266 (5)	20·067 (7)
β (°)	–	107·67 (2)	–
V (Å³)	286·4 (1)	1253·7 (4)	4272·2 (8)
Z	2	2	6
Space group	$I\bar{4}$	$P2_1/c$	$Pba2$
ρ_m (g cm⁻³)	3·16 (3)	3·24 (4)	4·80 (4)
ρ_x (g cm⁻³)	3·177	3·237	4·818
FW	274·0498	1222·2748	2066·4028
$F(000)$	256	1148	5388

an earlier short communication (Carpentier *et al.*, 1970), two other indium phosphorus chalcogenides exist which belong to the chalcogenohypodiphosphate family. The chemical compositions have been determined to be $In_4(P_2S_6)_3$ and $In_4(P_2Se_6)_3$. In the following, a characterization of the three indium phosphorus chalcogenides with respect to their structural chemistry is given including the refined crystal structure and absolute configuration of $InPS_4$, the quantitative crystal structure of $In_4(P_2S_6)_3$, and the qualitative crystal structure of $In_4(P_2Se_6)_3$.

Origin of specimens

Single crystals of the three indium phosphorus chalcogenides were obtained by chemical vapour transport experiments which were performed in evacuated quartz ampoules in a temperature gradient. Using iodine as a mineralizer and transporting agent the compounds were first synthesized from the elements in stoichiometric amounts by slowly heating ($100\,^{\circ}$C d^{-1}) the growth ampoules in a temperature gradient whereby the charge was kept in the cold end of the ampoules. In the case of $InPS_4$ the synthesis temperature was around $550\,^{\circ}$C, for the chalcogenohypodiphosphate compounds it was about $700\,^{\circ}$C. Crystal growth was initiated by reversing the temperature gradient in the growth ampoules. Bulk colourless single crystals of $InPS_4$ were obtained by chemical transport from 580 to $550\,^{\circ}$C (Nitsche & Wild, 1970). Light-greenish-yellow platelets of $In_4(P_2S_6)_3$ were grown from 700 to $620\,^{\circ}$C. Applying similar conditions we obtained single crystals of $In_4(P_2Se_6)_3$ in the form of dark-red platelets.

Crystal data

The chemical composition of the indium phosphorus chalcogenides was established by X-ray fluorescence analyses using InP, In_2S_3 and In_2Se_3 as standards. For the thiophosphate, atomic ratios In:P of 1:1 and In:S of 1:4 were found thus confirming the chemical formula as $InPS_4$. X-ray powder data of the yellow as well as the red crystal plates showed similarities to those of $Fe_2P_2S_6$ and $Fe_2P_2Se_6$ respectively. So it was suspected that the indium compounds belong to the chalcogenohypodiphosphate family. The In:P ratios were found to be 1:1·5 and the In:S(Se) ratios to be 1:4·5. Therefrom, the chemical formula was established as $In_4(P_2Ch_6)_3$ or $In_{1.33}P_2Ch_6$, indicating more evidently a metal-deficiency compared to the iron compounds.

$InPS_4$ crystallizes in space group $I\bar{4}$ (S_4^2) (Carpentier *et al.*, 1970). Precession photographs of $In_4(P_2S_6)_3$ crystals revealed monoclinic symmetry showing systematic extinctions $0k0$ with $k = 2n + 1$ and $h0l$ with

$l = 2n + 1$ whereby the space group was uniquely determined as $P2_1/c$ (C_{2h}^5). Normally exposed (about 2 h) precession photographs of $In_4(P_2Se_6)_3$ showed, at a first glance, trigonal symmetry. However, it was recognized by microscopic inspection in the conoscopic mode that the hexagon-like crystal plates were optically biaxial. This was contradictory to trigonal symmetry. Additional reflexions on long-time exposures (about 10 h) elucidated orthorhombic symmetry. Systematic extinctions $0kl$ with $k = 2n + 1$ and $h0l$ with $h = 2n + 1$ indicated the possible space groups $Pbam$ and $Pba2$. The latter was found to be correct since mirror symmetry could be excluded from geometrical considerations (see below).

Crystal data of the indium phosphorus chalcogenides are summarized in Table 1. The crystal densities were measured pycnometrically. Lattice constants were obtained from Guinier powder photographs using Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) with cubic As_2O_3 ($a = 11.081$ Å) as an internal standard. By grinding, powder samples for Guinier photographs were easily prepared for the brittle $InPS_4$, but were difficult to prepare for the soft and plastic plate-like species. However, chopping of the crystal plates with a razor blade resulted in powder diagrams with large numbers of sharp lines. Texture effects made it unreasonable to determine line intensities quantitatively. Thus, for $InPS_4$ only, line intensities were measured with a Zeiss–Jenoptik photometer and scaled to the value 100 for the strongest reflexion, whereas line intensities for the chalcogenohypodiphosphates are only given qualitatively as $s =$ strong, $m =$ medium, $w =$ weak. The powder spectra are listed in Table 2.

Intensity data collection

Needle-like specimens of $InPS_4$ were generally obtained as twins with [111] being the needle and twin axis (Carpentier *et al.*, 1970). For X-ray intensity measurements a sample with dimensions of $85 \times 85 \times 120$ µm was cleaved from a twin. A platy single crystal of $In_4(P_2S_6)_3$ with dimensions of $300 \times 150 \times 20$ µm was used. The crystal structure of $In_4(P_2Se_6)_3$ was not quantitatively determined (see below). In the case of $InPS_4$ intensity data of 753 independent reflexions in the range $0.0 \leq (\sin\theta)/\lambda \leq 1.1$ Å^{-1}, in the case of $In_4(P_2S_6)_3$ 2360 independent reflexions in the range $0.0 \leq (\sin\theta)/\lambda \leq 0.7$ Å^{-1}, were measured with a NaI(Tl) scintillation counter on the CAD-4 (Enraf–Nonius) automatic four-circle single-crystal diffractometer. Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71056$ Å) monochromatized by a graphite crystal was used. The background-corrected intensities were further corrected for absorption $\{\mu(InPS_4) = 55.8$ cm^{-1}, $\mu[In_4(P_2S_6)_3] = 54.1$ cm$^{-1}\}$ using the program *ORABS* (Busing, 1966). Lorentz and polarization corrections were performed

Table 2. *Powder data*

InPS$_4$

	h k l	I/I_o	d_c(Å)	d_o(Å)
1	1 0 1	100	4·7772	4·7799
2	0 0 2	5	4·5292	4·5288
3	1 1 0	15	3·9759	3·9803
4	1 1 2	85	2·9880	2·9875
5	1 0 3	32	2·6602	2·6594
6	2 1 1	59	2·4229	2·4229
7	2 0 2	15	2·3886	2·3885
8	2 2 0	20	1·9879	1·9874
9	1 1 4	5	1·9678	1·9671
10	2 1 3	23	1·9323	1·9320
11	3 0 1	9	1·8354	1·8356
12	2 2 2	3	1·8203	1·8203
13	3 1 0	4	1·7781	1·7782
14	2 0 4	28	1·7636	1·7642
15	1 0 5	5	1·7244	1·7251
16	3 1 2	14	1·6551	1·6556
17	3 0 3	4	1·5924	1·5918
18	3 2 1	5	1·5369	1·5368
19	2 1 5	2	1·4699	1·4688
20	1 1 6	6	1·4114	1·4113
21	4 0 0	6	1·4057	1·4055
22	3 1 4	3	1·3985	1·3982
23	3 2 3	7	1·3856	1·3859

In$_4$(P$_2$Se$_6$)$_3$

	h k l	I/I_o	d_c(Å)	d_o(Å)
1	1 $\bar{1}$ 1	m	8·662	8·689
2	2 $\bar{1}$ 0	w	7·256	7·257
3	2 $\bar{1}$ 1	m	6·825	6·839
4	0 0 3	s	6·689	6·690
5	1 $\bar{2}$ 0	m	5·327	5·332
6	1 $\bar{2}$ 1	m	5·149	5·148
7	2 $\bar{2}$ 1 / 4 0 1	m	4·670 / 4·668 } 4·675	
8	4 $\bar{1}$ 0	m	4·405	4·401
9	4 $\bar{1}$ 1	m	4·302	4·304
10	4 $\bar{1}$ 2	m	4·033	4·034
11	2 $\bar{2}$ 3	s	3·901	3·905
12	1 $\bar{3}$ 1 / 4 $\bar{2}$ 1 / 5 $\bar{1}$ 1	m	3·572 / 3·571 / 3·570 } 3·561	
13	2 $\bar{3}$ 1	m	3·400	3·404
14	6 0 1 / 1 $\bar{1}$ 6 / 2 0 6 / 5 $\bar{2}$ 0	w	3·160 / 3·158 / 3·158 / 3·157 } 3·150	
15	5 $\bar{2}$ 1	w	3·118	3·118
16	0 0 7 / 0 $\bar{2}$ 6 / 3 $\bar{1}$ 6	s	2·867 / 2·864 / 2·864 } 2·870	
17	4 $\bar{3}$ 2	m	2·811	2·805
18	2 $\bar{2}$ 6 / 1 $\bar{4}$ 0 / 0 4 6	m	2·744 / 2·744 / 2·744 } 2·737	
19	1 $\bar{4}$ 1	m	2·719	2·712
20	2 1 7 / 2 $\bar{4}$ 0 / 4 $\bar{1}$ 6 / 5 $\bar{3}$ 0 / 7 $\bar{1}$ 0	m	2·666 / 2·664 / 2·664 / 2·663 / 2·662 } 2·664	

+ 55 additional lines with multiple indexing

In$_4$(P$_2$S$_6$)$_3$

	h k l	I/I_o	d_c(Å)	d_o(Å)
1	0 $\bar{1}$ 1	w	9·008	9·015
2	0 0 2	m	8·702	8·723
3	0 $\bar{1}$ 2	s	6·707	6·752
4	1 0 0	s	6·519	6·525
5	1 $\bar{1}$ 2	m	5·340	5·343
6	0 $\bar{2}$ 1	s	5·039	5·042
7	1 $\bar{1}$ 3	w	4·651	4·655
8	0 $\bar{2}$ 2	w	4·504	4·510
9	0 0 4	m	4·351	4·359
10	1 0 4	m	4·266	4·262
11	1 $\bar{2}$ 1	m	4·168	4·171
12	1 2 0	w	4·095	4·097
13	1 $\bar{2}$ 2	s	4·012	4·015
14	1 $\bar{1}$ 4	s	3·953	3·947
15	1 $\bar{2}$ 1	m	3·827	3·827
16	1 $\bar{1}$ 3	m	3·574	3·576
17	0 3 1	m	3·440	3·444
18	1 $\bar{2}$ 4	m	3·314	3·315
19	2 0 0	m	3·260	3·260
20	2 1 $\bar{3}$	m	3·150	3·148
21	1 $\bar{3}$ 1	w	3·121	3·120
22	1 $\bar{1}$ 4	w	3·060	3·062
23	0 $\bar{3}$ 3	s	3·003	2·997
24	1 $\bar{3}$ 1	m	2·970	2·969
25	1 $\bar{2}$ 5	w	2·944	2·942

+75 additional lines with partially multiple indexing

with the XRAY 70 system of crystallographic programs (Stewart, Kundell & Baldwin, 1970).

Refinement and absolute configuration of the InPS$_4$ crystal structure

The crystal structure of InPS$_4$ was refined with In in position 2(a) (0,0,0), P in 2(d) $(0,\frac{1}{2},\frac{3}{4})$ and S in 8(g) (x,y,z) of space group $I\bar{4}$ (S_4^2) (No. 82 of *International Tables for X-ray Crystallography*, 1965), starting with the S positional parameters $x = 0·308$, $y = 0·233$, and $z = 0·131$ as reported by Carpentier *et al.* (1970) (where the S atom x and y parameters are inadvertently interchanged). Atomic scattering factors for the neutral atoms of In, P, and S were taken from Cromer & Waber (1965). $\Delta f'$ and $\Delta f''$ correction factors for anomalous dispersion (Cromer & Liberman, 1970) were also included in the structure calculations.

Table 3. *Positional parameters of the* InPS$_4$ *crystal structure* $(\times 10^4)$

	Position	x	y	z
In	2(a)	0	0	0
P	2(d)	0	5000	7500
S	8(g)	3057 (3)	2389 (3)	1302 (2)

A least-squares refinement was performed using the program *CRYLSQ* of the XRAY 70 system (Stewart *et al.*, 1970). The function minimized was $\Sigma w||F_o| - |F_c||^2$ with $w = 1/\sigma^2(F_o)$, σ being the estimated standard deviation (e.s.d.) derived from counting statistics. 207 reflexions had F_o values less than three times their e.s.d.'s and were treated as 'less-thans' in the structure refinement. Refinement of the earlier published model (Carpentier *et al.*, 1970) using individual anisotropic

temperature coefficients (Cruickshank, 1956) and an isotropic correction factor for secondary extinction (Larson, 1967) yielded a reliability index $R (= \Sigma ||F_o| - |F_c||/\Sigma F_o)$ of 0·038 with 'less-thans' omitted and $\bar{R} =$ 0·060 with 'less-thans' included. Starting from the centrosymmetrically related model and applying an identical refinement procedure an R value of 0·045 was obtained without and 0·068 with 'less-thans' included. Different weighting schemes were applied to the observed structure factors. The R value was lowest with unit weights.*

Comparing the results for both models we see that the R value for the second model is about 18% higher than that for the first model. This remarkable difference led to the conclusion that the first model represents the absolute configuration of the InPS$_4$ crystal structure, the final positional and anisotropic thermal parameters of which are summarized in Table 3. A difference Fourier map calculated with these parameters was completely featureless.

Sulphur packing, coordination and lattice constants indicate close relationships between the crystal structure of InPS$_4$ and zinc blende. In fact, the former can be considered as a zinc blende derivative. Starting from the doubled cubic zinc blende unit cell and the chemical formula $M_4^{II}S_4$ one can follow a pathway to InPS$_4$ which is illustrated in Fig. 2. Modification of the chemical composition to $M_2^I M_2^{III} S_4$ results in the chalcopyrite-type structure of CuFeS$_2$. With $M_3^I M^V S_4$ one obtains the crystal structure of famatinite, Cu$_3$SbS$_4$ (Gaines, 1957). Continuing the substitution to $M_2^I M^{III} M^{IV} S_4$ the stannite-type structure is obtained. If CdGa$_2$S$_4$ is written as $\Box M^{II} M_2^{III} S_4$ ($\Box$ represents a metal vacancy) the crystal structure of cadmium gallium sulphide (Hahn, Frank, Klingler, Stoerger & Stoerger, 1955) also turns out to be a zinc blende derivative with one M sublattice missing. Extending the terminology further one arrives at InPS$_4$ which can be represented

The crystal structure of InPS₄ (a zinc blende derivative)

The crystal structure of indium thiophosphate is built up by a puckered cubic close-packed arrangement of S atoms with S layers parallel to ($\bar{1}12$), as shown in Fig. 1. The In and P atoms are both tetrahedrally coordinated by S. The coordination tetrahedra are connected by corner sharing. Bonding distances and angles of the coordination polyhedra are listed in Table 4. The In—S as well as the P—S bonding distances are closely covered by the sum of the corresponding covalent radii (In 1·44, P 1·06, S 1·02 Å).

* Lists of structure factors for both configurations of InPS$_4$ and for In$_4$(P$_2$S$_6$)$_3$, and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33243 (69 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
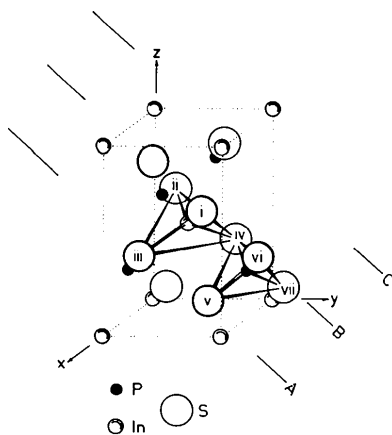
Table 4. *Bond lengths* (Å) *and angles* (°) *in the* InPS$_4$ *crystal structure*

Coordinates of bonding atoms

In	$x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{4}$	S^{iv}	$\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{4} - z$
P	$x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{4}$	S^{v}	$\bar{x}, \bar{y}, z$
S^I	$\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$	S^{vi}	$\frac{1}{2} + y, \frac{3}{2} - x, \frac{1}{4} - z$
S^{II}	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$	S^{vii}	$x, y + 1, z$
S^{III}	$\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{4} - z$		

InS$_4$ tetrahedron

In—S$^{(I-Iv)}$ 2·480 (2)
S$^{(I,II)}$—In—S$^{(III,Iv)}$ 103·07 (6)
S^I—In—S^{II} }
S^{III}—In—S^{Iv} }   123·20 (6)

PS$_4$ tetrahedron

P—S$^{(Iv-vii)}$ 2·043 (2)
S$^{(Iv,vI)}$—P—S$^{(v,vii)}$ 106·37 (8)
S^{iv}—P—S^{vi} }
S^v—P—S^{vii} }   115·86 (8)

Fig. 1. Coordination tetrahedra in the InPS$_4$ crystal structure.
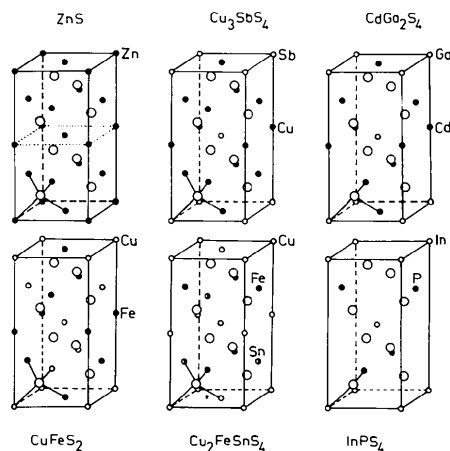

Fig. 2. The crystal structure of InPS$_4$ as a derivative of the zinc blende structure (all atoms are at, or close to, multiples of $\frac{1}{8}$).

as $\square_2 M^{III} M^V S_4$ indicating a zinc blende derivative with two metal sublattices missing. In all these compounds the S atoms are tetrahedrally coordinated. Whereas, in general, this coordination tetrahedron is formed by four M atoms there are three M atoms and one M vacancy in the $CdGa_2S_4$ structure and two M atoms and two M vacancies in the $InPS_4$ structure.

The crystal structure of $In_4(P_2S_6)_3$ (a defect $Fe_2P_2S_6$-type structure)

It was suspected from the similarity of the powder spectra of $Fe_2P_2S_6$ and $In_4(P_2S_6)_3$ that there must exist close crystal structural relationships between both compounds. This is also supported by a comparison of the lattice constants [for convenient comparison $In_4(P_2S_6)_3$ is set up in $P2_1/a$]:

$Fe_2P_2S_6$ (Klingen, Eulenberger & Hahn, 1973)	$In_4(P_2S_6)_3$
Space group $C2/m$	Space group $P2_1/a$
$a = 5\cdot934\,(6)$ Å	$a = 18\cdot266\,(5)$ Å
$b = 10\cdot28\,(1)$	$b = 10\cdot528\,(2)$
$c = 6\cdot772\,(7)$	$c = 6\cdot842\,(2)$
$\beta = 107\cdot2\,(1)°$	$\beta = 107\cdot67\,(2)°$
$V = 395\,(1)$ Å^3	$V = 1253\cdot7\,(4)$ Å^3.

The $In_4(P_2S_6)_3$ unit cell is a threefold supercell of $Fe_2P_2S_6$ with the a parameter tripled. Thus, the chemical formula of indium thiohypodiphosphate is best represented by $In_{1\cdot33}\square_{0\cdot67}P_2S_6$ ($\square$ being the symbol for an indium vacancy). Accommodation of $In_{1\cdot33}P_2S_6$ in the $Fe_2P_2S_6$ unit cell leaves one third of the M sites unoccupied. The threefold supercell results from an ordering of the metal vacancies. Thereby, the space group is changed from $C2/m$ to $P2_1/a$.

Starting values for one third of the $In_4(P_2S_6)_3$ unit-cell content were taken from the $Fe_2P_2S_6$ crystal structure (Klingen *et al.*, 1973) with x parameters divided by three. The remaining atoms were obtained by adding $\frac{1}{3},0,0$ and $\frac{2}{3},0,0$ to the positional parameters of this first set of atoms. A three-dimensional F_0^2 (Patterson) synthesis could be completely interpreted on the basis of this structural model. The crystal structure was refined in the internationally standardized space group $P2_1/c$ (C_{2h}^5) (No. 14 of *International Tables*, 1965) with all atoms in the general position $4(e)$. Thus, one had to refine the positional parameters of two inequivalent In atoms, three inequivalent P atoms, and nine inequivalent S atoms, giving a total of 42 positional parameters. With anisotropic thermal coefficients (Cruickshank, 1956), a correction factor for isotropic extinction (Larson, 1967) and a scale factor, 128 parameters had to be refined. $\Delta f'$ and $\Delta f''$ correction factors for anomalous dispersion (Cromer & Liberman, 1970) were also applied. Refinement resulted in a final R value of 0·063 with 1033 'less-thans'

omitted and 0·097 with 'less-thans' included. The positional and thermal parameters of the crystal structure of $In_4(P_2S_6)_3$ are listed in Table 5. With these parameters no significant features were detected on a ΔF synthesis.*

Bond lengths and angles of the different InS_6 and P_2S_6 coordination polyhedra are comprehensively given in Table 6 (for the labelling of atoms see Fig. 5). The average In—S bonding distance of 2·657 Å is practically covered by the sum of the ionic radii (In^{3+} 0·81, S^{2-} 1·84 Å). It follows from the bonding angles that the InS_6 octahedra are distinctly distorted. The average P—S bonding distance of 2·028 Å is close to the sum of the pertinent covalent radii (P 1·06, S 1·02 Å).

---

* See deposition footnote on p. 1100.

Table 5. *Positional parameters of the* $In_4(P_2S_6)_3$ *crystal structure* ($\times 10^4$) [*all atoms in position* $4(e)$]

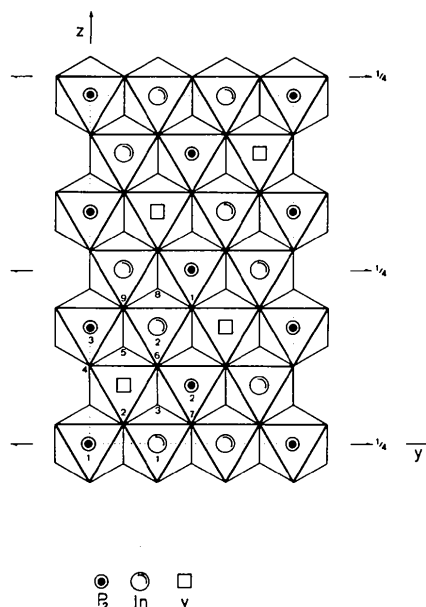|	x	y	z
In(1)	24 (3)	3199 (2)	120 (1)
In(2)	17 (3)	3495 (2)	3237 (1)
P(1)	1706 (9)	23 (5)	161 (3)
P(2)	1697 (9)	5129 (6)	1851 (3)
P(3)	1702 (9)	80 (6)	3538 (3)
S(1)	2462 (10)	5104 (6)	4180 (4)
S(2)	2622 (10)	1550 (6)	847 (3)
S(3)	7410 (10)	3468 (6)	862 (4)
S(4)	2523 (9)	173 (6)	2567 (3)
S(5)	7412 (9)	1740 (5)	2543 (3)
S(6)	2610 (10)	3510 (6)	2445 (4)
S(7)	2454 (9)	5045 (6)	837 (3)
S(8)	7482 (9)	3426 (6)	4186 (3)
S(9)	2476 (9)	1735 (5)	4162 (3)

Fig. 3. S—S double layer around P_2, In and metal vacancy (v) in $x \sim 0$ showing the connexion of the coordination octahedra (idealized) in the $In_4(P_2S_6)_3$ crystal structure.

Table 6. *Bond lengths (Å) and angles (°) in the* $In_4(P_2S_6)_3$ *crystal structure*

Coordinates of bonding atoms

In(1)	x,y,z	S(1^{iii})	$\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$	S(6^{ii})	$\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$
In(2)	x,y,z	S(2^{i})	x,y,z	S(7^{i})	x,y,z
P(1^{i})	x,y,z	S(2^{ii})	$\bar{x},\bar{y},\bar{z}$	S(7^{ii})	$\bar{x}, 1 - y, \bar{z}$
P(1^{ii})	$\bar{x},\bar{y},\bar{z}$	S(3^{i})	$x - 1, y, z$	S(7^{iii})	$\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$
P(2^{i})	x,y,z	S(3^{ii})	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	S(8^{i})	$x - 1, \frac{1}{2} - y, z - \frac{1}{2}$
P(2^{ii})	$\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$	S(4^{i})	x,y,z	S(8^{ii})	$x - 1, y, z$
P(3^{i})	x,y,z	S(4^{ii})	$x - 1, \frac{1}{2} + y, \frac{1}{2} - z$	S(8^{iii})	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
P(3^{ii})	$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$	S(5^{i})	$x - 1, y, z$	S(9^{i})	x,y,z
S(1^{i})	x,y,z	S(5^{ii})	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	S(9^{ii})	$x, \frac{1}{2} - y, z - \frac{1}{2}$
S(1^{ii})	$x, \frac{1}{2} - y, z - \frac{1}{2}$	S(6^{i})	x,y,z	S(9^{iii})	$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$

In(1)S$_6$ octahedron

In(1)–S(2^{i})	2·550 (6)
–S(3^{i})	2·566 (8)
–S(7^{i})	2·634 (6)
–S(7^{ii})	2·747 (6)
–S(8^{i})	2·657 (6)
–S(9^{ii})	2·768 (7)

S(2^{i})–In(1)–S(7^{i})	90·47 (19)
–S(3^{i})	106·69 (22)
–S(7^{ii})	170·91 (24)
–S(9^{ii})	83·48 (21)
–S(8^{i})	96·51 (19)
S(7^{i})–In(1)–S(3^{i})	95·26 (21)
–S(7^{ii})	89·67 (18)
–S(9^{ii})	83·31 (20)
–S(8^{i})	170·36 (20)
S(3^{i})–In(1)–S(7^{ii})	82·34 (20)
–S(9^{ii})	169·77 (18)
–S(8^{i})	89·11 (21)
S(7^{ii})–In(1)–S(9^{ii})	87·51 (19)
–S(8^{i})	82·39 (18)
S(9^{ii})–In(1)–S(8^{i})	90·87 (20)

In(2)S$_6$ octahedron

In(2)–S(1^{i})	2·624 (6)
–S(4^{ii})	2·597 (6)
–S(5^{i})	2·613 (6)
–S(6^{i})	2·608 (8)
–S(8^{ii})	2·801 (8)
–S(9^{i})	2·719 (6)

S(1^{i})–In(2)–S(6^{i})	87·36 (22)
–S(9^{i})	83·17 (18)
–S(5^{i})	168·56 (23)
–S(8^{ii})	90·11 (21)
–S(4^{ii})	96·65 (19)
S(6^{i})–In(2)–S(9^{i})	87·29 (20)
–S(5^{i})	102·39 (21)
–S(4^{ii})	97·61 (21)
–S(8^{ii})	175·64 (18)
S(9^{i})–In(2)–S(5^{i})	91·24 (17)
–S(4^{ii})	175·09 (23)
–S(8^{ii})	88·88 (19)
S(5^{i})–In(2)–S(8^{ii})	79·78 (20)
–S(4^{ii})	88·06 (18)
S(8^{ii})–In(2)–S(4^{ii})	86·21 (20)

P(1), 1S$_6$ octahedron

P(1^{i})–P(1^{ii})	2·228 (8)
P(1^{i})[P(1^{ii})]–S(2^{i})[S(2^{ii})]	2·019 (8)
–S(8^{iii})[S(8^{i})]	2·038 (8)
–S(1^{ii})[S(1^{iii})]	2·014 (8)
S(2^{i})[S(2^{ii})]–S(8^{i})[S(8^{iii})]	3·885 (8)
–S(1^{iii})[S(1^{ii})]	3·784 (10)
S(1^{iii})[S(1^{ii})]–S(8^{iii})[S(8^{i})]	3·859 (9)

S(2^{i})[S(2^{ii})]–P(1^{i})[P(1^{ii})]–S(8^{iii})[S(8^{i})]	108·38 (34)
–S(1^{ii})[S(1^{iii})]	119·35 (41)
S(8^{iii})[S(8^{i})]–P(1^{i})[P(1^{ii})]–S(1^{ii})[S(1^{iii})]	111·58 (39)
P(1^{ii})[P(1^{i})]–P(1^{i})[P(1^{ii})]–S(2^{i})[S(2^{ii})]	106·46 (37)
–S(8^{iii})[S(8^{i})]	102·37 (35)
–S(1^{ii})[S(1^{iii})]	107·22 (32)

P(2), 3S$_6$ and P(3), 2S$_6$ octahedra

P(2^{i})[P(3^{i})]–P(3^{ii})[P(2^{ii})]	2·217 (8)
P(2^{i})[P(2^{ii})]–S(6^{i})[S(6^{ii})]	2·012 (8)
–S(7^{i})[S(7^{iii})]	2·071 (8)
–S(5^{ii})[S(5^{i})]	2·016 (8)
P(3^{ii})[P(3^{i})]–S(4^{iii})[S(4^{i})]	2·020 (8)
–S(9^{iii})[S(9^{i})]	2·061 (8)
–S(3^{i})[S(3^{ii})]	2·012 (8)
S(6^{i})[S(6^{ii})]–S(3^{i})[S(3^{ii})]	3·844 (8)
–S(4^{iii})[S(4^{i})]	3·917 (8)
S(7^{i})[S(7^{iii})]–S(3^{i})[S(3^{ii})]	3·842 (10)
–S(9^{iii})[S(9^{i})]	3·814 (9)
S(5^{ii})[S(5^{i})]–S(4^{iii})[S(4^{i})]	3·855 (9)
–S(9^{iii})[S(9^{i})]	3·812 (8)

S(6^{i})[S(6^{ii})]–P(2^{i})[P(2^{ii})]–S(7^{i})[S(7^{ii})]	108·98 (39)
–S(5^{ii})[S(5^{i})]	114·99 (34)
S(7^{i})[S(7^{iii})]–P(2^{i})[P(2^{ii})]–S(5^{ii})[S(5^{i})]	114·26 (40)
S(3^{i})[S(3^{ii})]–P(3^{ii})[P(3^{i})]–S(9^{iii})[S(9^{i})]	115·30 (32)
–S(4^{ii})[S(4^{i})]	113·67 (40)
S(4^{ii})[S(4^{i})]–P(3^{ii})[P(3^{i})]–S(9^{iii})[S(9^{i})]	110·57 (38)
P(3^{ii})[P(3^{i})]–P(2^{i})[P(2^{ii})]–S(6^{i})[S(6^{ii})]	106·07 (36)
–S(7^{i})[S(7^{iii})]	103·62 (31)
–S(5^{ii})[S(5^{i})]	107·97 (36)
P(2^{ii})[P(2^{i})]–P(3^{i})[P(3^{ii})]–S(4^{i})[S(4^{ii})]	105·18 (31)
–S(9^{i})[S(9^{iii})]	103·08 (35)
–S(3^{ii})[S(3^{i})]	107·93 (37)

The crystal structure of indium thiohypo-diphosphate consists of a cubic-close-packed arrangement of S atoms with P_2 groups and In atoms in octahedral interstices of the packing. The connexion of the coordination octahedra by edge sharing as well as the distribution of the metal vacancies around $x = 0$ is shown in Fig. 3, adopting an idealized presentation similar to that used by Klingen et al. (1973). The apices of the octahedra are formed by the S atoms. The packing of the S layers is illustrated in Fig. 4 viewed along [010]. The cation-free S–S double layer is responsible for the perfect cleavability observed parallel to (100). Fig. 5 was drawn schematically to clarify the bonding relationships of Table 6.*

The crystal structure of $In_4(P_2Se_6)_3$ (a defect $Fe_2P_2Se_6$-type structure)

The powder spectrum of $In_4(P_2Se_6)_3$, compared to that of $Fe_2P_2Se_6$, exhibits very similar features but has a

---

* During the investigation of the structural chemistry of indium phosphorus chalcogenides we became aware of a paper by Soled & Wold (1976) giving a qualitative derivation of the In thiohypo-diphosphate crystal structure from a comparison with that of $Mn_2P_2S_6$. Their idealized structural model is in substantial agreement with our results.
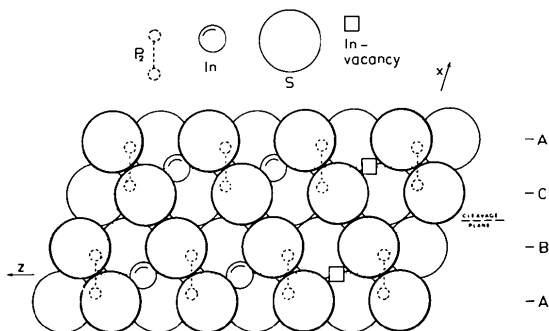

Fig. 4. The crystal structure of $In_4(P_2S_6)_3$ viewed along [010] showing the cubic close packing of S atoms.
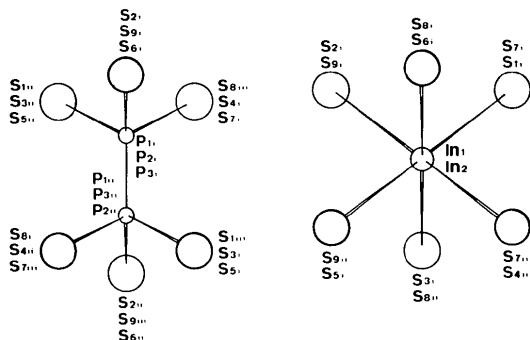

Fig. 5. P_2S_6 and InS_6 coordination polyhedra with labelling of atoms (to be used in connexion with Table 6).

large number of additional lines which could all be indexed on the basis of a large orthorhombic unit cell. The lattice constants of indium selenohypodiphosphate are geometrically related to those of $Fe_2P_2Se_6$ as follows:

$Fe_2P_2Se_6$
(Klingen et al., 1973)
Space group $R3$ (C_3^4)
$a = 6.265$ (6) Å

$c = 19.80$ (2)
$V = 673.0$ (5) Å³

$In_4(P_2Se_6)_3$

Space group $Pba2$ (C_{2v}^8)
$A = 19.197$ (9) Å
$B = 11.090$ (9)
$C = 20.067$ (7)
$V = 4272$ (1) Å³.

With the approximation $A \sim 3a$, $B \sim a\sqrt{3}$, $C \sim c$, the mutual transformation of both vector sets is given in matrix form as:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 3 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ -\frac{1}{6} & \frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix}$$

from which approximate positional parameters of the $In_4(P_2Se_6)_3$ structure can be derived.

In analogy to the S compound it was concluded that $In_4(P_2Se_6)_3$ is also a metal-deficient hypodiphosphate compound and is to be described as $In_{1.33}\square_{0.67}P_2Se_6$. It builds up a sixfold superstructure of that of $Fe_2P_2Se_6$; this is clear from a comparison of the unit-cell volumes. The slightly elongated c axis indicates that the hexagonal-close-packed arrangements of Se atoms (Klingen et al., 1973) in the two crystal structures are identical.

Since mirror symmetry would lead to an unreasonable atomic arrangement (two adjacent Se–Se double layers, absurd P–P distances, and a lining up of M and M-vacancies in the z direction) the existence of a mirror plane must be excluded. Thus, the space group of the $In_4(P_2Se_6)_3$ crystal structure can be given uniquely as $Pba2$ (C_{2v}^8) (No. 32 of International Tables, 1965). The unit cell contains $Z = 18 \times In_{1.33}\square_{0.67}P_2Se_6 = 6 \times In_4\square_2(P_2Se_6)_3$, i.e. a total of 24 In, 36 P, and 108 Se atoms and 12 metal vacancies. In addition, with anisotropic thermal coefficients, far more than 300 parameters would have to be refined in the crystal structure analysis. To save computer time we decided to perform no quantitative structure analysis for $In_4(P_2Se_6)_3$. In the following a qualitative description of the crystal structure is presented which is compatible with space group $Pba2$.

Approximate positional parameters of the atoms can be calculated from the parameters of the $Fe_2P_2Se_6$ crystal structure using the transformation matrix given above. To obtain adequate values the origin of the $Fe_2P_2Se_6$ unit cell has to be moved from the triad of
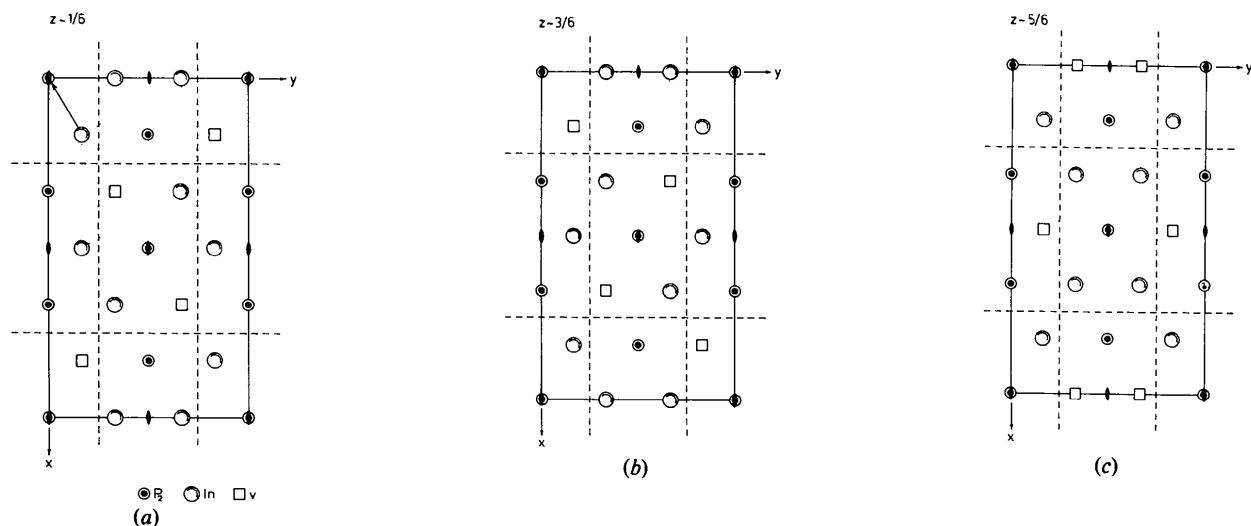
Fig. 6. Distribution of metal vacancies (v) in the $In_4(P_2Se_6)_3$ crystal structure at (a) $z \sim \frac{1}{6}$, (b) $z \sim \frac{3}{6}$, (c) $z \sim \frac{5}{6}$; the Se atoms have been omitted for clarity.

space group $R3$ by $\frac{1}{6},\frac{1}{6},0$ to the diad of space group $Pba2$ as indicated in Fig. 6(a). If the unit cell of $In_4(P_2Se_6)_3$ is outlined using this new origin, a distribution of the metal vacancies in $z \sim \frac{1}{6}$ results, which is identical to the vacancy distribution in $x \sim 0$ of the crystal structure of the S compound. The 'location' of the metal vacancies in the $In_4(P_2Se_6)_3$ crystal structure in $z \sim \frac{1}{6}$, $\frac{3}{6}$, and $\frac{5}{6}$ is shown schematically in Fig. 6. 'Coordinates' of the metal vacancies are summarized as follows: four vacancies at position 4(c) (x,y,z) with $x \sim \frac{2}{6}$, $y \sim \frac{2}{6}$, $z \sim \frac{1}{6}$; four vacancies at position 4(c) (x,y,z) with $x \sim \frac{1}{6}$, $y \sim \frac{1}{6}$, $z \sim \frac{3}{6}$; four vacancies at position 4(c) (x,y,z) with $x \sim \frac{3}{6}$, $y \sim \frac{1}{6}$, $z \sim \frac{5}{6}$. The In atoms have the same z parameters as these vacancies. For a given z value the x and y parameters of the In atoms are those belonging to the remaining two z parameters of the vacancies listed above ($e.g.$ $\frac{1}{6},\frac{1}{6},\frac{1}{6}$; $\frac{3}{6},\frac{1}{6},\frac{1}{6}$ $etc.$).

Indium selenohypodiphosphate exhibits a typical layer structure which is schematically illustrated in Fig. 7. The perfect cleavage of the plate-like single crystals is understood from the occurrence of metal-free Se double layers in the hexagonal-close-packed arrangement of Se atoms.

Note added in proof: A paper by Katty, Soled & Wold (1977) has since been published dealing with the crystal growth and some crystal data of $In_{2/3}PSe_3[=In_4(P_2Se_6)_3]$.
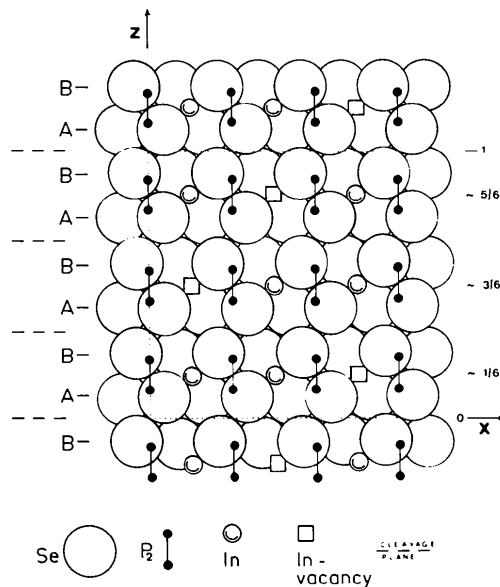

Fig. 7. Stacking of Se layers in the $In_4(P_2Se_6)_3$ crystal structure.

The authors have found it to be trigonal, space group $R3$, with $a = 6\cdot37$ and $c = 19\cdot86$ Å. These lattice constants indicate that there is no ordering between the In atoms and vacancies. Although crystal-growth experiments were performed by the authors at temperatures about 100°C lower than our crystal-growth temperatures, it appears doubtful that an ordering does not occur in the Se compound whereas it is observed in the S compound. The authors may possibly have overlooked the weak superstructure reflections on the precession photographs of $In_{2/3}PSe_3$.

References

BITHER, T. A., DONOHUE, A. C. & YOUNG, H. S. (1971). *J. Solid State Chem.* **3**, 300–304.

BUCK, P. & CARPENTIER, C. D. (1973). *Acta Cryst.* B29, 1864–1868.

BUSING, W. R. (1966). Oak Ridge National Laboratory, Tennessee, USA.

CARPENTIER, C. D. (1974). Thesis, Univ. of Freiburg.

CARPENTIER, C. D., DIEHL, R. & NITSCHE, R. (1970). *Naturwissenschaften*, **57**, 393–394.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747–753.

DIEHL, R. & CARPENTIER, C. D. (1976). *Acta Cryst.* B32, 1399–1404.

GAINES, R. V. (1957). *Am. Mineral.* **42**, 766–779.

GARIN, J. & PARTHÉ, E. (1972). *Acta Cryst.* B28, 3672–3674.

HAHN, H., FRANK, G., KLINGLER, W., STOERGER, A. D. & STOERGER, G. (1955). *Z. Anorg. Allg. Chem.* **279**, 241–270.

International Tables for X-ray Crystallography (1965). Vol. I, 2nd ed. Birmingham: Kynoch Press.

ISAACS, T. J., GOTTLIEB, M. & FEICHTNER, J. D. (1974). *Appl. Phys. Lett.* **24**, 107–109.

KATTY, A., SOLED, S. & WOLD, A. (1977). *Mater. Res. Bull.* **12**, 663–666.

KLINGEN, W., EULENBERGER, G. & HAHN, H. (1973). *Z. Anorg. Chem.* **401**, 97–112.

KLINGEN, W., OTT, R. & HAHN, H. (1973). *Z. Anorg. Allg. Chem.* **396**, 271–278.

LARSON, H. (1967). *Acta Cryst.* **23**, 664–666.

NITSCHE, R. & WILD, P. (1970). *Mater. Res. Bull.* **5**, 419–423.

SOKALOV, A. I. & NECHAEVA, V. V. (1969). *Izv. Akad. Nauk SSSR Neorg. Mater.* **5**, 989.

SOLED, S. & WOLD, A. (1976). *Mater. Res. Bull.* **11**, 657–662.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

WEISS, A. & SCHAEFER, H. (1960). *Naturwissenschaften*, **47**, 495.

WEISS, A. & SCHAEFER, H. (1963). *Z. Naturforsch.* **18**, 81–82.

ZIMMERMANN, H., CARPENTIER, C. D. & NITSCHE, R. (1975). *Acta Cryst.* B31, 2003–2006.

The Crystal Structure of Triclinic WO₃

BY ROLAND DIEHL AND GERNOT BRANDT

Institut für Angewandte Festkörperphysik der Fraunhofer-Gesellschaft, Eckerstrasse 4, D-7800 Freiburg im Breisgau, Federal Republic of Germany

AND EKHARD SALJE

Mineralogisches Institut der Technischen Universität, Welfengarten 1, D-3000 Hannover, Federal Republic of Germany

Between *ca* −40 and 17°C tungsten trioxide, WO_3, has a pseudocubic triclinic crystal structure, space group $P\bar{1}$ (C_i^1), with $a = 7\cdot309$ (2), $b = 7\cdot522$ (2), $c = 7\cdot678$ (2) Å, $\alpha = 88\cdot81$ (2), $\beta = 90\cdot92$ (2), $\gamma = 90\cdot93$ (2)°, $V = 421\cdot93$ (9) Å³, and $Z = 8$. Intensity data for 2452 independent X-ray reflections from a single-domain crystal were measured on an automatic four-circle single-crystal diffractometer. From analogies with the crystal structure of the monoclinic room-temperature modification of WO_3, the triclinic crystal structure was determined and refined to $R = 0\cdot050$. It is characterized by corner-sharing, and distorted and tilted WO_6 octahedra with a tilting component around each of the coordination axes. The W atoms are off-centre in the O octahedra and close to an O triangle, giving three short and three long W—O bonding distances.

Introduction

From 0 up to 1200 K stoichiometric tungsten trioxide, WO_3, is reported to undergo not less than eight phase transformations in the solid state (Levkowitz, Dowell & Shields, 1975; Rao & Rao, 1974). Crystallographic information has become available on the WO_3 phases which occur between 900 and −70°C during cooling. Below 900°C, WO_3 is tetragonal, space group $P4/nmm$ (D_{4h}^7) (Kehl, Hay & Wahl, 1952) and