The Crystal Structure of SnP

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The crystal structure of SnP can be described with a trigonal unit cell of dimensions $a = 4.3922(7)$ and $c = 6.040(3)$ Å and spacegroup $P\bar{3}m1$, $Z = 2$. The structure is layered and similar to the C6 structure from which it can be formally derived by substitution of the octahedrally coordinated atoms with atom pairs. The tin atoms form a hexagonal packing. The phosphorus atoms are situated as P_2 pairs filling octahedra in every second tin layer. The closest Sn–Sn distance is 3.482(2) Å. The distances between the atoms of the P_2 pairs are 2.2 Å, and the closest Sn–P distances are 2.62–2.67 Å.   © 1990 Academic Press, Inc.

Introduction

The existence of a tin monophosphide at ordinary pressures was first reported by Katz *et al.* (*1*). These authors also characterized the phase as trigonal. The possible spacegroups were stated as $P321$, $P3m1$, or $P\bar{3}m1$. The unit cell had the dimensions $a = 8.78$ and $c = 5.98$ Å.

High pressure modifications of SnP with other structure types have been reported by Osugi *et al.* (*2*) and Donohue (*3*). Olofsson (*4*) tried to repeat the preparation of the modification at ordinary pressure and performed several experiments with heat treatments of mixtures of tin and red phosphorus at temperatures between 300 and 500°C but found only some weak lines at *d*-values close to the strongest lines reported for SnP as the only indication of the existence of such a phase. Vivian (*5*) reported

from metallographic examinations of the tin-phosphorus system a eutectic between Sn_4P_3 and Sn_3P_4 at 50 at. %.

The present work confirms in principle the observations reported in Refs. (*1, 4*, and *5*). The apparent contradiction in these reports obviously are results of metastability, most probably caused by high nucleation energy of SnP compared to those of adjacent phases in the Sn–P system. The present work concerns the synthesis of SnP and the determination of its crystal structure.

Experimental Techniques

Synthesis of SnP

SnP was synthesized by heating a two-g mixture of tin and red phosphorus with the composition 52 at. % P at 610°C in a silica tube, followed by slow cooling in the furnace to room temperature. The cooling rate was 0.8°C/min down to 250°C and then gradually slower until room temperature

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was reached. The reaction vessel was evacuated and sealed and had a volume of about 5 cm³.

Examination of the Reaction Product

The reaction product was examined by X-ray powder diffraction using a Hägg-Guinier focusing camera, with $CuK\alpha_1$ radiation and silicon ($a = 5.431065$ Å) as an internal calibration standard, and by optical metallographical methods. An examination with the use of Mössbauer spectroscopy has also been performed and will be reported elsewhere (6).

Single Crystal X-Ray Diffraction

A fragment of the reaction product, with the approximate dimensions 480 × 130 × 275 μm³, was examined using a Weissenberg camera.

Intensity data from 671 reflections were collected with a Stoe–Philips computer-controlled four-circle single-crystal diffractometer equipped with a graphite monochromator to yield $MoK\alpha$ radiation. An ω–2θ step-scan technique was used, and three test reflections were measured at regular intervals to check the crystal orientation and the stability of the instrument.

Experimental Results

General Properties of the Synthesis Product

The reaction product was dark grey and exhibited a perfect cleavage in one direction as if the whole piece was one single crystal (1). The cleavage surfaces had a metallic luster.

A small amount of unreacted phosphorus was also in the reaction vessel used for the synthesis. The phosphorus content of the gray part of the sample was therefore concluded to correspond to a composition near to SnP as the gross composition of the initial charge was 52 at. % phosphorus.

From other syntheses from mixtures of tin and phosphorus with approximate compositions of 50 at. %, the present author has found that SnP was not always formed when melts with similar compositions were cooled. Instead a mixture of Sn_4P_3 and Sn_3P_4 was often formed. In these cases the reaction product had a eutectic type of structure, as shown by metallographic examination similar to that reported by Vivian (5). Further details of the metallographical studies will be presented elsewhere (7). Attempts to obtain SnP from reactions in the solid state between red phosphorus and tin in the temperature range 400–520°C have not been successful (cf., Ref. (4)).

Metallographic and X-Ray Powder Diffraction Examinations

Metallographic examination of the dark gray reaction product indicated the existence of a single phase.

A powder pattern obtained by X-ray powder diffraction could be indexed by the use of a hexagonal cell with the dimensions $a = 4.3922$ and $c = 6.060$ Å (Table I). The perfect cleavage of SnP, somewhat similar to mica after crushing and grinding, gave reasons to assume that the intensities in Table I were affected by orientation effects. This assumption was later verified by comparison with single crystal X-ray diffraction intensities. In Table II the powder data given by Ref. (1) are interpreted in terms of a mixture of SnP and Sn_4P_3 (4).

X-Ray Single Crystal Examination

Several fragments of the SnP sample were examined by the use of a Weissenberg camera. Most small fragments were, however, very distorted by plastic deformation and cracks originating from cleavage. Attempts to avoid the deformation effects by crushing samples under liquid nitrogen were not successful.

Finally a piece with the approximate dimensions 480 × 130 × 275 μm was chosen.

TABLE I

POWDER DIFFRACTION DATA FOR SnP

I	h k l	Q_{obsd}	Q_{calcd}
w	1 0 0	0.06898	0.06912
m	1 0 1	0.09642	0.09652
vvw	0 0 2	0.10954	0.10963
w	1 0 2	0.17880	0.17875
m	1 1 0	0.20731	0.20735
vvw	1 1 1	0.23436	0.23476
vvw	2 0 0	0.27707	0.27646
w	2 0 1	0.30399	0.30387
w	1 1 2	0.31703	0.31699
vvw	2 0 2	0.38586	0.38609
vvw	1 1 3	0.45403	0.45401
vvw	2 1 0	0.48372	0.48381
vvw	2 1 1	0.51127	0.51122
vvw	2 0 3	0.52344	0.52313
vvw	2 1 2	0.59474	0.59344
vvw	3 0 0	0.62298	0.62204
vvw	2 0 4	0.71731	0.71498
vvw	2 1 3	0.73066	0.73048

Note. $Q = 1/d^2$ (Å^{-2}). $a = 4.3922(7)$ Å, $c = 6.040(3)$ Å.

It was also cracked but the diffracted rays from different parts of the specimen diverged by such a small angle that X-ray diffraction data collected from this "single crystal" was expected to contain enough information to make an elucidation of the structure possible. The intensities of 671 reflections were measured. Absorption and Lp corrections were performed ($\mu = 131.8$ cm^{-1}) using seven surfaces to describe the crystal with the use of the program ABSSTOE (9). The calculated transmission factors were between 10 and 26% for all reflections.

From the 671 measured reflections averages were calculated for equivalent reflections assuming Laue symmetry $\bar{3}m$ according to rotation and Weissenberg photographs in agreement with the symmetry assumption in Ref. (1). The averages were calculated using the program AVEJO (9) which gave 199 independent reflections

with an agreement factor between equivalent reflections $R = 0.14$ based on F^2.

Crystal Structure Determination

The crystal structure was determined in two steps. The coordinates of the tin atoms were first obtained from the Patterson function calculated for the ($\bar{1}$ 1 0) plane. The atomic parameters of the phosphorus atoms were obtained from calculations of electron densities based on observed F-values and difference synthesis. The spacegroup chosen for the description was No. 164, $P\bar{3}m1$.

The refinement of the structure model was performed with the least-squares program UPALS (9). The refined parameters were atomic coordinates not fixed by symmetry, an overall scale factor, individual isotropic temperature factors for all atoms, and an occupancy factor for the phos-

TABLE II

POWDER DIFFRACTION DATA FOR SnP ACCORDING TO KATZ *et al.* (1) COMPARED WITH DATA FROM THIS WORK AND Sn$_4$P$_3$ ACCORDING TO OLOFSSON (4)

SnP (1)			SnP (this work)			Sn$_4$P$_3$ (4)		
h k l	d	I	h k l	d	I	h k l	d	I
0 0 1	5.97	vvw	Not observed					
2 0 0	3.77	m	1 0 0	3.808	w			
2 0 1	3.19	vs	1 0 1	3.220	m			
0 0 2	2.99	m−	0 0 2	3.021	vvw			
2 1 0	2.91	vvw				0 0 12	2.945	m−
1 0 2	2.82	m−				1 0 7	2.842	vs
2 0 2 3 0 1	2.35	s	1 0 2	2.365	w			
2 2 0	2.18	s	1 1 0	2.1963	m			
3 1 0	2.09	w	1 1 1	2.0657	vvw			
0 0 3	2.001	w				1 0 14	2.035	s
3 1 1	1.973	vw				1 1 0	1.986	s
4 0 0	1.890	w	2 0 0	1.8998	vvw			
4 0 1	1.804	m+	2 0 1	1.8137	w			
2 2 2	1.768	m	1 1 2	1.7760	w			
4 1 1	1.598	w	2 0 2	1.6099	vw			
2 2 3	1.477	m−	1 1 3	1.4841	vvw			
4 2 0	1.433	vw	2 1 0	1.4378	vvw			
4 2 1 2 0 4	1.394	m+	2 1 1	1.3985	vw			
			2 0 3	1.3822	vvw			
4 2 2	1.296	w	2 1 2	1.2967	vvw			
6 0 0	1.269	vvw	3 0 0	1.2670	vvw			
4 0 4	1.177	w	2 0 4	1.1807	vvw			
4 2 3	1.166	w	2 1 3	1.1699	vw			

TABLE III

THE STRUCTURAL DATA OF SnP FROM THE
LAST REFINEMENT CYCLE

Space group: $P\bar{3}m1$
Hexagonal cell: $a = 4.3922(7)$
$c = 6.040(3)$
$V = 100.9 \text{ Å}^3$
$Z = 2$
Calculated density: 4.92 g/cm^3

	x	y	z	G	$B(\text{Å}^2)$
Sn	$\frac{1}{3}$	$\frac{2}{3}$	0.3025(2)	$\frac{1}{6}$	1.40(3)
P1	0	0	0.185(2)	0.042(4)	1.0(3)
P2	0.863(1)	$1 - x$	0.054(1)	0.115(5)	1.0(2)

$R_w = 0.171$ (based on F^2)
$R = 0.068$
$S = 1.006$

Note. The atoms are situated in the $2d$, $2c$, and $6i$ positions with the parameter values, where B values are isotropic temperature factors. The least-squares line through 198 points with ABS(ΔR) < 4.0 has the slope 1.00 and y intercept $= -0.21$. There was one observation outside the range.

phorus atoms. The results of the refinement are given in Table III.

Description of the Structure

SnP exhibits a typical layered structure since it consists of molecules which are infinitely extended in two dimensions. These are loosely stacked on top of each other to form three-dimensional crystals. The spacegroup chosen for the description is $P\bar{3}m1$. The tin atoms are located in the position $2d$ which leads to a hexagonal stacking. The octahedral voids formed by the stacking are of two kinds, filled or empty.

All octahedron surfaces which are normal to the trigonal axis are equilateral triangles with the length of the sides equal to the length of the a-axis, i.e., 4.392 Å.

Furthermore the empty octahedra have six surfaces which are isosceles triangles with two sides having the lengths 3.482 Å. These distances represent the Sn–Sn con-

tacts between the sandwiches consisting of two hexagonal tin layers with filled octahedral voids.

The filled octahedra have six surfaces which are isosceles triangles with two sides of lengths 4.448 Å, i.e., similar to the length of the third side, 4.392 Å, which means that these triangles are almost equilateral. Hence the filled octahedra are nearly regular.

The filled octahedra can contain two phosphorus atoms, each of which is bonded to the other and to three tin atoms constituting vertices of the octahedron. In this way the phosphorus atoms obtain tetrahedral coordination. The almost regular octahedra are through this arrangement held together by P_2 pairs since both P atoms are bonded to three tin atoms in the corners of opposite triangles in the octahedra.

The P_2 pairs are situated in two different crystallographic positions which are both partially occupied. P1 is situated in a position of type $2c$ which is 25% occupied, and P2 is occupying 23% of a $6i$ position which leads to a filling of octahedra with diatomic molecules having four different orientations.

This type of filling of octahedra is topologically similar to the arrangement in the pyrite structure, which can be formally described in terms of Fe-octahedra filled with S_2 pairs (Fig. 1). The pyrite structure can be
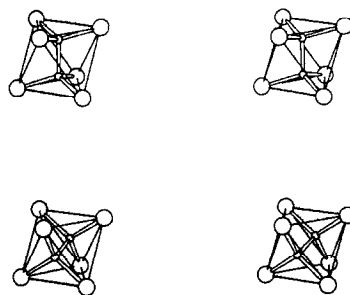

FIG. 1. Stereoscopic pairs of anion octahedra filled with cation pairs in two different orientations.

TABLE IV

INTERATOMIC DISTANCES SHORTER THAN 3.5 Å WITH STANDARD DEVIATIONS

Kind of atom	Distance (Å)
Sn–3 Sn	3.482(2)
Either	
Sn–1 P1	2.633(4)
Sn–1 P2	2.668(6)
Sn–1 P1	2.620(8)
Or	
Sn–3 P1	2.668(6)
P1–1 P1	2.23(3)
P1–3 Sn	2.634(4)
P2–1 P2	2.19(1)
P2–1 Sn	2.619(8)
P2–2 Sn	2.669(6)

Note. For number of close neighbors, see text.

formally derived through filling of all octahedral voids with diatomic molecules in a cubic close-packed lattice.

SnP can analogously be described as filling of one-half of the octahedral voids with P_2 pairs in a hexagonal close-packed tin lattice.

With this formalistic description SnP can be geometrically related to the anti-CdI_2 structure in the same way as pyrite can be related to the rock salt structure.

Within the Sn–P–P–Sn sandwiches the P–P distances are 2.2 Å and the Sn–P distances are about 2.65 Å. The closest atomic distances between the four-layer sandwiches are Sn–Sn distances of 3.483 Å (Table IV).

Discussion

The tin phosphide SnP reported by Katz *et al.* (*1*) was obviously the same phase as the one described in the present paper. The reason for their finding of an *a*-axis twice the size of the present is probably the existence of Sn_4P_3 in the sample prepared in Ref. (*1*) of which four of the strongest diffraction lines have been indexed in terms of a unit cell for SnP. This is illustrated in Table II.

The SnP structure is closely related to structures which are known for other monopnictides of group XIV elements and for monochalcogenides of group XIII elements viz. SiP, GaTe, GaS, and GaSe. These structures have been extensively discussed by Hulliger (*10*) who pointed out that the preference of sp^3 bonds and the composition of such compounds lead to "cation pairs" unless half of the cations are monovalent as in the TlSe-type compounds and that the cation pairs usually "induce a layer structure." These layer structures can, as indicated above, be conveniently discussed in the terminology used for structures topologically described in terms of filling of voids in the packing of spheres. The atom pairs (e.g., the P_2 groups in SnP) are known to be accommodated in trigonal prismatic or octahedral voids. The packing sequences can then be described and compared with the well-known structures of MoS_2 (C7), CdI_2 (C6), $CdCl_2$ (C19), and CdI_2 (C27). The SnP structure can in these terms be described as derived from the C6 type.

The filled octahedral voids in the C6-type structure are occupied by P_2 pairs in SnP which seem to be disordered with respect to their orientations. The octahedra formed by the Sn atoms are nearly regular. The P_2 pairs appear to be equally distributed between the four different orientations in which they can link two opposing triangles in an octahedron.

Concerning the stoichiometry it can be seen from Table III that the experimentally determined composition of the crystal examined is found to be $SnP_{0.94(4)}$, i.e., less than two standard deviations from SnP. The GaTe, SiAs, and SiP structures can be derived from the CdI_2 structures (C6 and

C27, respectively) with the cation pairs in distorted anion octahedra (*10*). Due to the distortion of the octahedra the symmetries of these phases are monoclinic and orthorhombic, respectively. The trigonal symmetry of SnP may be associated with a suitable size factor between tin and phosphorus permitting the Sn octahedra to be nearly regular and filled with P_2 pairs with four different orientations. No signs of a superstructure caused by ordering of the P_2 pairs were observed in the single crystal diffraction pattern.

The structure model for a compound of the SnP type with the atomic pairs all oriented parallel with the *c*-axis has been predicted by Hulliger (*10*).

It is reasonable to assume that the orientation of the P_2 pairs within the complex layers of filled octahedra are not completely random. A possible way to get an ordered arrangement is obtained by doubling the *a*-axis. In this way the P_2 pairs can be described using two different crystallographic sites, and an order similar to that found in layers of the pyrite structure can be obtained. No such order could, however, be deduced from the single crystal or powder diffraction photographs. No extra reflections from ordering appeared from powder diffraction photographs of powder that had been annealed at 150°C for 9 days. The disorder is therefore interpreted as stacking faults in the sequence of the sandwiches composed of filled octahedra.

Although no order of the type described was obtained, the number of neighbor atoms given in Table IV is based on the assumption of local order of the type mentioned above.

The SnP structure shows some similarities with the structures of Sn_4P_3 and SnP_3. Some details of the SnP structure can be seen as intermediates between the two other structures which are of a more and a less metallic type, respectively. In Sn_4P_3 there are no P–P contacts and the Sn–Sn contact distances 3.250 Å are much smaller than the corresponding distances 3.483 Å in SnP. In SnP_3 on the other hand the catenation of phosphorus has extended to P_6 rings with no Sn–Sn contacts.

The existence of the SnP structure can be seen in the light of the similarities and differences between the Sn–P and the Sn–As system where SnAs is known to crystallize with the NaCl-type structure which is reported for a high-pressure modification of SnP (*3*). The normal pressure modification of SnP therefore can be considered as a borderline case between the structures of lighter elements forming layer structures of the present type and more metallic structures with higher coordination formed by heavier elements.

Acknowledgments

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