CONTRIBUTION NO. 1573 FROM THE CENTRAL RESEARCH DEPARTMENT,
E. I. DU PONT DE NEMOURS AND COMPANY, EXPERIMENTAL STATION, WILMINGTON, DELAWARE 19898

The Synthesis, Structure, and Superconducting Properties of New High-Pressure Forms of Tin Phosphide

BY P. C. DONOHUE

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Reactions of Sn and P in a tetrahedral anvil press at conditions ranging from 15 to 65 kbars and 600 to 1300° gave intimate mixtures of two new forms of SnP: a tetragonal form having cell dimensions $a = 3.831 \pm 0.001$ Å and $c = 5.963 \pm 0.001$ Å and a cubic rock salt type having $a = 5.5359 \pm 0.0001$ Å at 25°. The crystal structure of the tetragonal phase was refined from powder diffraction intensity data and shown to be similar to that of high-pressure GeP and GeAs. The tetragonal form transformed slowly and irreversibly to the cubic form when heated at ambient pressure between 100 and 200°. Meissner-effect measurements showed the tetragonal form to be normal to 1.25°K and the cubic form to be superconducting between 2.8 and 4.0°K.

Introduction

In the Sn–P system, only the compounds SnP[1] and Sn_4P_3[2] are known. Both have hexagonal crystal structures. Osugi, *et al.*,[3] reported the formation of sphalerite-type SnP at 1600–1800° and 40–50 kbars. The powder pattern,[4] however, was the same as that reported herein for NaCl-type SnP.

Experimental Section

All reactions were run in a tetrahedral anvil press of National Bureau of Standards design[5] using a cylindrical boron nitride crucible approximately 0.6 cm long and 0.125 cm^3 in volume, surrounded by a graphite-sleeve resistance heater inserted in a pyrophyllite tetrahedron. The temperature was measured using a Pt–Rh thermocouple uncorrected for pressure effects and placed at the center of the surface of the cylinder. The temperature at the ends is approximately 30% lower. The operating procedure has been explained elsewhere.[6]

High-purity Sn filings were obtained from a metal rod and passed through a magnet to remove impurity from the file. These were mixed with powdered P and pelleted. Several reactions were run at various conditions. In general, the reactants were cold pressured, then brought to temperature, held for 1 or 2 hr, cooled for about 2 hr, and quenched to room temperature in less than 1 min while pressure was maintained.

All products were characterized by Debye–Scherrer X-ray powder diffraction at 25°. Films were read on a David Mann film reader, Model No. 1222. Unit cell dimensions were refined by a least-squares method with the Nelson–Riley function as one parameter.

Electrical resistivities were measured by a four-probe technique described previously.[7] Superconducting transition temperatures were measured by observing the Meissner effect at temperatures above 1.25°K.

Results

Filings of Sn were mixed with powdered P in the Sn:P atomic ratio of 1:(0.9–1.1) and treated at the conditions of 800° and 65 kbars, holding 1 hr, cooling 3 hr to 500°, and quenching. Reactions were also run at 1200° and 65 kbars and at 900° and 15 kbars. The products of all reactions showed similar Debye–Scherrer patterns. Two phases were present, a major tetragonal phase and a minor cubic phase. The Debye–Scherrer pattern of the major phase (Table I) was indexed on the basis of a tetragonal cell: $a = 3.831 \pm 0.001$ Å, $c = 5.963 \pm 0.001$ Å. The weaker lines were indexed on the basis of a cubic cell: $a = 5.5359 \pm 0.0001$ Å. The reflections of the cubic cell were analogous to those of SnAs[8] but shifted to indicate a smaller cell.

The mixture of tetragonal and cubic phases, when heated in air at ambient pressure, transformed slowly and irreversibly to the cubic phase between 100 and 200°. A broad, shallow endotherm was seen in the dta of several samples. On a few samples the transition could not be seen in the dta.

Resistivity measurements on a polycrystalline piece of SnP which was composed predominantly of the tetragonal form showed metallic behavior: $\rho_{25°C} = 2 \times 10^{-5}$ ohm cm, $\rho_{4.2°K} = 3 \times 10^{-6}$ ohm cm. Meissner effect was measured on both the tetragonal and cubic forms. The tetragonal form did not show a superconducting transition to 1.25°K; the cubic form showed a superconducting transition temperature between 2.8 and 4.8°K.

Experiments under similar conditions but starting with an Sn:P ratio of 1:2 generally yielded the same mixture of tetragonal and cubic SnP and black P.

Crystal Structure Analysis

The crystal structure of the tetragonal phase was refined from powder intensity data. The structure is similar to that of high-pressure GeP and GeAs.[9] Intensity data were gathered from a diffractometer tracing by obtaining relative weights of the peaks. A Norelco diffractometer using Cu Kα radiation and a LiF bent crystal monochromator was used. A scanning rate of 0.25°/min was used with the chart scaled to 1 in./deg. A smooth background curve was drawn and the peaks were traced onto Cronaflex drafting film,

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Table I

X-Ray Powder Diffraction Pattern of Tetragonal SnP ($a = 3.831 \pm 0.001$ Å, $c = 5.963 \pm 0.001$ Å)

I/Ic*	h	k	l	d (obs.)	d (calc.)
90	1	0	1	3.2169	3.2226
100	0	0	2	2.9784	2.9810
90	1	1	0	2.7105	2.7084
90	1	1	2	2.0030	2.0046
80	2	0	0	1.9151	1.9152
70	1	0	3	1.7625	1.7640
80	2	1	1	1.6458	1.6464
70	2	0	2	1.6103	1.6113
20	0	0	4	1.4901	1.4905
30	2	2	0	1.3545	1.3542
30	1	1	4	1.3066	1.3056
30	2	1	3	1.2972	1.2975
10	3	0	1	1.2473	1.2465
30	2	2	2	1.2332	1.2310
40	3	1	0	1.2111	1.2113
20	2	0	4	1.1756	1.1762
10	1	0	5	1.1361	1.1385
40	3	1	2	1.1224	1.1221
10	3	0	3	1.0744	1.0742
10	3	2	1	1.0462	1.0459
10	2	2	4	1.0018	1.0023
20	2	1	5	.9784	.9786
10	4	0	0	.9577	.9576
10	3	1	4	.9408	.9400
10	3	2	3	.9376	.9369
5	4	1	1	.9186	.9179
10	4	0	2	.9123	.9117
10	3	3	0	.9026	.9028
2	2	0	6	.8816	.8820
5	3	0	5	.8715	.8714
10	3	3	2	.8645	.8640
10	4	2	0	.8569	.8565
10	4	1	3	.8422	.8416
10	1	0	7	.8318	.8314
10	4	2	2	.8231	.8232
5	3	2	5	.7930	.7932

*Read using the David Mann Film Reader.

Table II

I_o and I_c for Tetragonal SnP

h	k	l	I_o	I_c
1	0	1		47.36
−1	0	−1		44.06
			100.00	91.43
0	0	2		20.93
0	0	−2		22.13
			36.95	43.07
1	1	0	72.23	74.84
1	1	2		25.67
−1	−1	−2		27.16
			55.41	52.83
2	0	0	26.59	25.77
1	0	3		13.19
−1	0	−3		11.95
			21.70	25.14
2	1	1		14.25
−2	−1	−1		13.36
			25.70	27.61
2	0	2		12.41
−2	0	−2		13.16
			27.71	25.57
0	0	4		1.68
0	0	−4		1.86
			3.99	3.54
2	2	0	7.60	7.76
1	3	0	12.79	10.45
1	2	3		9.32
−1	−2	−3		8.41
1	1	4		4.26
−1	−1	−4		4.72
			25.60	26.71
3	0	1		2.90
−3	0	−1		2.72
			6.50	5.61
2	0	4		3.01
−2	0	−4		3.34
			6.10	6.35

No. IDF4, cut out, and weighed. Fourteen pieces of data were collected.

Least-squares refinement based on the function $\Sigma w I_o - I_c|^2$ was done using a program written by Prewitt[10] which handles the sums of nonequivalent overlapping reflections. Atomic scattering factors[11] corrected for the real and imaginary parts of the anomalous dispersion were used. The imaginary component was applied separately to reflections *hkl* and $\bar{h}\bar{k}\bar{l}$. Occupancy factors were held at 2 and the weighting scheme $w = 1/\sigma^2$, with $\sigma = \sqrt{I_o} + 2.0$, was used. The positions 0, 0, z of space group I4mm were used in the refinement with z held at 0.0 for Sn and $z = 0.4$ initially assumed for P.

One scale factor, the single position parameter for P, and two isotropic temperature factors were varied. The R factor defined as $R = \Sigma I_o - I_c/\Sigma I_o$ was reduced to 7.8%. The intensity data and final position parameters are shown in Table II. Bond distances were calculated[12] (Table III). The numbers of the atoms correspond to those in Figure 1.

Table III

Final Parameters and Bond Distances and Angles for Tetragonal SnP

Atom	Position (x, y, z)	Temp factor, Å²
Sn	0, 0, 0	0.9 ± 0.3
P	0, 0, 0.428 ± 0.010	2.6 ± 1.6

Atoms[a]	Dist, Å	Atoms	Angles, deg
Sn(1)–P(2)	2.55 ± 0.06	P(3)–Sn(1)–P(2)	99.0 ± 1.2
Sn(1)–P(3)	2.74 ± 0.01	P(3)–Sn(1)–P(4)	81.0 ± 1.2
Sn(1)–P(4)	3.41 ± 0.06	P(5)–Sn(1)–P(3)	88.6 ± 0.4

[a] The numbers on the atoms correspond to the numbers of the atoms in Figure 1.

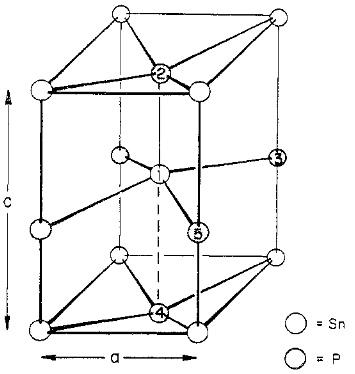

Figure 1.—Structure of SnP.

The cubic structure was shown to be NaCl type. Intensities were read from a Debye–Scherrer pattern using the David Mann film reader. These were compared to the Debye–Scherrer patterns calculated for SnP having the NaCl-type and ZnS-type structures by a program written by Jeitschko and Parthé.[13] The results (Table IV) clearly indicate the NaCl-type structure to be correct. The pattern is similar to that reported by Osugi, *et al.*,[4] to be sphalerite type.

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(10) C. T. Prewitt, local unpublished computer program.

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TABLE IV

DEBYE–SCHERRER PATTERN OF NaCl-TYPE SnP AND CALCULATED INTENSITIES FOR NaCl-TYPE AND SPHALERITE-TYPE SnP (λ(Cu Kα) 1.54178 Å, $a = 5.535 \pm 0.001$ Å)[a]

I/Io obs.	h	k	l	d (obs.)	d (calc.)	I calc. (NaCl type)	I calc. (Sphalerite type)
90	1	1	1	3.2177	3.1955	84	159
100	2	0	0	2.7748	2.7674	123	44
85	2	2	0	1.9599	1.9568	89	89
50	3	1	1	1.6703	1.6688	38	68
45	2	2	2	1.5998	1.5977	31	11
20	4	0	0	1.3847	1.3837	14	14
15	3	3	1	1.2704	1.2698	15	27
40	4	2	0	1.2377	1.2376	38	14
25	4	2	2	1.1300*	1.1298	29	32
10	5	1	1	1.0649*	1.0651	9	16
15	4	4	0	.9784*	.9784	11	11
15	5	3	1	.9357*	.9355	16	29
20	6	0	0	.9225*	.9224	5	2
20	6	2	0	.8751*	.8751	24	24
5	5	3	3	.8441*	.8440	10	17
15	6	2	2	.8343*	.8344	29	11
						R = 18.4%	R = 51.0%

[a] Asterisks signify λ(Cu Kα_1) 1.54051 Å.

Discussion

The formation of two new high-pressure forms of SnP has been shown. It is unclear which phase is the more stable at 65 kbars and why the two phases are intimately mixed. X-Ray diffraction at high pressure may perhaps resolve the phase relationships. The cubic phase should be the high-pressure phase since the density is greater. The calculated density of the cubic phase is 5.860 g/cm^3 while the calculated density of the tetragonal phase is 5.68 g/cm^3. The cubic form may be present at high pressure and upon quenching may revert partially to the tetragonal phase. The transformation from tetragonal to cubic upon heating at atmospheric pressure is interesting since it involves a transformation from a less dense to a more dense phase.

The crystal structure of the tetragonal phase has been shown to be similar to that of high-pressure GeP and GeAs.[9] The structure (Figure 1) is related to the NaCl type by a small shifting of atoms. If the diagonal on the basal plane equaled the c axis and $z = 0.5$, the structure would be NaCl type. The atoms are in a distorted octahedral arrangement having one short bond, four slightly longer equal bonds, and one long bond. The shift to the cubic structure involves a regularization of the octahedron. The crystal structure of SnAs[8] is known to be NaCl type and implies that as the elements become more metallic the NaCl-type structure is favored. Both forms of SnP are metallic conductors. This may be because the compounds have one extra electron for conduction. The tetragonal forms of GeP and GeAs showed superconductivity;[9] however, only the cubic SnP was seen to be superconducting above 1.25° K.

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AND THE ISTITUTO DI CHIMICA ANALITICA ED ELETTROCHIMICA OF THE UNIVERSITY OF PISA, PISA, ITALY

A Kinetic Study of the Reaction of Arsenic Acid with Iodide Ions

BY F. SECCO, A. INDELLI, AND P. L. BONORA

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The rate of the reaction of arsenic acid with potassium iodide was studied at 25.0° and at ionic strengths 0.200, 0.300, and 3.00 M. The rate equation, obtained by a statistical treatment of the data, is $V = k_1[H^+][H_3AsO_4][I^-] + k_2[H^+]^2[H_3AsO_4]\cdot[I^-] + k_3[H^+]^2[H_3AsO_4][I^-]^2$. The reaction shows very low salt effects even in the presence of Ba^{2+} ions. The catalytic effect of iron(II) and copper(I) ions was also investigated. The reaction mechanism is discussed.

The reaction between arsenate and iodide ions in acidic media was studied by several authors[1-4] by different techniques, but until now a satisfactory interpretation of the results has not been given either because the experimental methods[1] were inadequate or because it was not the main object of the research.[2-4] Roebuck[1] was able to show that the reaction orders extrapolated to zero concentration of the reactants were unity for every reactant and greater than unity for I$^-$ and for H$^+$ in more concentrated solutions of these ions. Liebhafsky[3] and Bobtelsky and Rosowskaja-Rossienskaja[5] arrived at the same conclusion.

Experimental Section

The chemicals used for the kinetics were $Na_2HAsO_4\cdot 7H_2O$ (Erba RP), KI (Erba RP), and $HClO_4$ (Erba RP, 60%). The sodium perchlorate used to keep the ionic strength, I, constant in part was a BDH LR product purified by recrystallization and in part was prepared from $HClO_4$ and Na_2CO_3 (Erba RP) and then recrystallized twice from water. $NaClO_4$ was standardized by neutralization after it passed through acidic ion-exchange resin.

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