

The Crystal Structure of SnP_3 and a Note on the Crystal Structure of GeP_3

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SnP_3 crystallizes in the trigonal space group $R\bar{3}m$ with six formula units in a unit cell of dimensions $a = 7.378 \text{ \AA}$ and $c = 10.512 \text{ \AA}$. The detailed atomic arrangement has been determined from three-dimensional single crystal X ray data.

The structure is characterized as a layer structure related to the As-type structure (A7). The identical layers consist of puckered P_6 rings connected by Sn atoms. The centers of the P_6 rings are situated between Sn atoms of adjacent layers. This leads to a distorted octahedral coordination for the tin atoms with three phosphorus atoms belonging to the same layer as the tin atom at a distance of 2.662 \AA , and three phosphorus atoms in an adjacent layer at a distance of 2.925 \AA . The P-P bond length within the rings is 2.222 \AA and the P-P-P bond angle is 99.1° .

Introduction

One of the present authors (1) has reported powder data for $\text{Sn}_{0.3}\text{P}$. This phase has now been further studied by single crystal X-ray diffraction methods and it has been found that the ideal crystallographic formula is SnP_3 . In Ref. 1 it was also noted that X-ray powder data given by Donohue and Young (6) for GeP_3 indicated that the high pressure phase GeP_3 probably has the same structure as SnP_3 . This has now been confirmed by a least-squares refinement of the powder data from Ref. 6.

Experimental

Preparation. The synthesis was performed in two stages as described in Ref. 1. The nominal composition was SnP_4 and the final heat treatment was undertaken for 2 days at 575°C followed by slow cooling to room temperature. The sample so obtained had a silicon-like appearance (2) with visible traces of red phosphorus.

X-ray investigation. Phase analysis and a determination of the unit cell dimensions was carried out by X-ray powder methods using a Guinier-Hägg focussing camera with $\text{CuK}\alpha_1$ radiation. Silicon ($a = 5.43054 \text{ \AA}$) was used as an internal standard. The single crystal investigation

was performed with the equi-inclination Weissenberg method using zirconium-filtered $\text{MoK}\alpha$ radiation and the multiple film technique. Thin iron foils were interleaved between successive films. The intensities were estimated visually by comparison with a calibrated intensity scale. The intensities were corrected for Lorentz and polarization factors. Atomic scattering factors and the real part of the anomalous dispersion correction were taken from Ref. 3.

The calculations were carried out in part on an IBM 1800 computer and partly on a CDC 3600 computer using the programs CELSIUS, DRF, LALS, and DISTAN. The programs have been described briefly elsewhere (4).

Determination and Refinement of the SnP_3 Structure

The single crystal used was very irregular in shape. It was therefore considered that an attempt to correct for absorption would hardly provide any significant improvement in the intensity data. The errors due to absorption are furthermore rather small due to the smallness of the crystal, which measured less than $0.04 \times 0.06 \times 0.10 \text{ mm}$ [$\mu(\text{MoK}\alpha) = 61 \text{ cm}^{-1}$]. The crystal was rotated about the [100] direction in the nonprimitive hexagonal unit cell which will

be used in the following. Only general reflexions with $-h + k + l = 3n$ were observed indicating a rhombohedral lattice. No special conditions were observed, and as no condition limiting the occurrence of special reflexions could be found, translational elements of symmetry could be excluded. The Laue symmetry was found to be $\bar{3}m$; there are therefore three possible space groups: $R32$, $R3m$ and $R\bar{3}m$. The structure was determined on the basis of the nonprimitive hexagonal unit cell and it could be shown that all vectors in the Patterson projection $P(V, W)$ could be explained by six tin atoms in the $6(c)$ position and eighteen phosphorus atoms in the $18(h)$ position. Comparison of electron densities based on calculated and observed structure factors respectively confirmed the proposed structure and gave improved positional parameters and scale factors. These values were then used in a least-squares refinement. The parameters refined were atomic coordinates, individual isotropic temperature factors and three scale factors, one for each of the three layer lines ($0kl$), ($1kl$) and ($2kl$). The weighting scheme of Cruickshank et al. (5), $w = 1/(a + |F_0| + c|F_0|^2 + d|F_0|^3)$, was used with the values $a = 70$, $c = 0.007$, and $d = 0.0001$. The refinement was stopped when the discrepancy factor $R = \sum ||F_0| - |F_c|| / \sum |F_0|$ was 0.093 for the 245 independent F values. The final structural description of SnP_3 is as follows: Space group $R\bar{3}m (D_{3d}^5)$; Hexagonal cell with $a = 7.3785(5)$ Å; $c = 10.5125(11)$ Å; $U = 495.65$ Å³; $Z = 6$. Calculated density: 4.25 g cm⁻³. The atoms are in the $6(c)$ and the $18(h)$ positions with the parameter values:

Atom	x	y	z	$B(\text{Å}^2)$
Sn $6(c)$	0	0	0.2576(1)	0.45(8)
P $18(h)$	0.5139(4)	0.4861(4)	0.2828(3)	0.56(8)

The limits of error given for the atomic parameters are the standard deviations obtained from the least-squares refinement. Interatomic distances and bond angles are given in Table I and observed and calculated structure factors in Table II.

Refinement of the GeP_3 Structure

The powder diffraction intensities of GeP_3 published by Donohue and Young (6) were corrected for Lorentz and polarization factors and used for computing the Patterson section $P(0, V, W)$. This gave approximate starting

TABLE I

INTERATOMIC DISTANCES (Å UNITS) AND ANGLES WITH STANDARD DEVIATIONS IN SnP_3 . DISTANCES SHORTER THAN 3.3 Å ARE LISTED

Sn-3P	2.662(3)
3P	2.925(3)
P-2P	2.222(4)
P-Sn-P	70.65(8)
P-Sn-P	94.69(4)
P-Sn-P	97.31(13)
P-Sn-P	161.78(12)
Sn-P-Sn	161.78(12)
Sn-P-P	98.21(13)
Sn-P-P	93.57(12)
P-P-P	99.08(22)

coordinates for a least-squares refinement. The final coordinates obtained from the refinement were, for Ge: [0, 0, 0.269(5)] and for P: [0.515(8), 0.485(8), 0.282(5)]. Standard deviations of atomic coordinates are given in parentheses. The discrepancy factor as defined above is 0.136.

Description and Discussion of the SnP_3 Structure

SnP_3 represents a new structure type, the main features of which have been predicted by Donohue and Young for the isostructural GeP_3 (6). The structure of SnP_3 can be described as a layer structure related to the As-type structure in which the corrugated layers are composed of puckered P_6 rings as shown in Fig. 1. The layers thus formed are stacked upon one another perpendicular to the c axis so that a distorted octahedral environment of phosphorus atoms is formed around each of the tin atoms. Hence, the tin atoms have six phosphorus neighbors; three within the layer at a distance of 2.662(3) Å and three in an adjacent layer at a distance of 2.925(3) Å. The corresponding distances in GeP_3 are 2.50(5) and 2.85(6).

Phosphorus has been reported to have the As type structure above 50 kbars (9). The cell dimensions of this form are $a = 3.3777$ Å and $c = 8.806$ Å. The distance corresponding to the hexagonal a axis of the As-type phosphorus can be found in the P_6 rings of SnP_3 . This distance was found to be 3.382(4) Å.

In a recent survey of metal polyphosphides (7), a simple formula was derived for calculating the oxidation number of the metal atoms in poly-

TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$). REFLEXIONS NOT INCLUDED IN THE REFINEMENT ARE MARKED WITH AN ASTERISK.
REFLEXIONS TOO WEAK TO BE MEASURED ARE NOT LISTED

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	0	0	1631	1602	0	0	0	565	513	1	1	1	581	579
0	0	0	1739	1709	0	0	0	1123	1093	1	1	1	1326	1296
0	0	0	1748	1718*	0	0	0	1125	1095	1	1	1	1328	1298
0	0	0	1750	1720*	0	0	0	1127	1097	1	1	1	1330	1300
0	0	0	1815	1785	0	0	0	1190	1160	1	1	1	1393	1363
0	0	0	1823	1793	0	0	0	1198	1168	1	1	1	1401	1371
0	0	0	1825	1795	0	0	0	1199	1169	1	1	1	1402	1372
0	0	0	1828	1798	0	0	0	1202	1172	1	1	1	1405	1375
0	0	0	1829	1799	0	0	0	1203	1173	1	1	1	1406	1376
0	0	0	1832	1802	0	0	0	1206	1176	1	1	1	1409	1379
0	0	0	1833	1803	0	0	0	1207	1177	1	1	1	1410	1380
0	0	0	1834	1804	0	0	0	1208	1178	1	1	1	1411	1381
0	0	0	1835	1805	0	0	0	1209	1179	1	1	1	1412	1382
0	0	0	1836	1806	0	0	0	1210	1180	1	1	1	1413	1383
0	0	0	1837	1807	0	0	0	1211	1181	1	1	1	1414	1384
0	0	0	1838	1808	0	0	0	1212	1182	1	1	1	1415	1385
0	0	0	1839	1809	0	0	0	1213	1183	1	1	1	1416	1386
0	0	0	1840	1810	0	0	0	1214	1184	1	1	1	1417	1387
0	0	0	1841	1811	0	0	0	1215	1185	1	1	1	1418	1388
0	0	0	1842	1812	0	0	0	1216	1186	1	1	1	1419	1389
0	0	0	1843	1813	0	0	0	1217	1187	1	1	1	1420	1390
0	0	0	1844	1814	0	0	0	1218	1188	1	1	1	1421	1391
0	0	0	1845	1815	0	0	0	1219	1189	1	1	1	1422	1392
0	0	0	1846	1816	0	0	0	1220	1190	1	1	1	1423	1393
0	0	0	1847	1817	0	0	0	1221	1191	1	1	1	1424	1394
0	0	0	1848	1818	0	0	0	1222	1192	1	1	1	1425	1395
0	0	0	1849	1819	0	0	0	1223	1193	1	1	1	1426	1396
0	0	0	1850	1820	0	0	0	1224	1194	1	1	1	1427	1397
0	0	0	1851	1821	0	0	0	1225	1195	1	1	1	1428	1398
0	0	0	1852	1822	0	0	0	1226	1196	1	1	1	1429	1399
0	0	0	1853	1823	0	0	0	1227	1197	1	1	1	1430	1400
0	0	0	1854	1824	0	0	0	1228	1198	1	1	1	1431	1401
0	0	0	1855	1825	0	0	0	1229	1199	1	1	1	1432	1402
0	0	0	1856	1826	0	0	0	1230	1200	1	1	1	1433	1403
0	0	0	1857	1827	0	0	0	1231	1201	1	1	1	1434	1404
0	0	0	1858	1828	0	0	0	1232	1202	1	1	1	1435	1405
0	0	0	1859	1829	0	0	0	1233	1203	1	1	1	1436	1406
0	0	0	1860	1830	0	0	0	1234	1204	1	1	1	1437	1407
0	0	0	1861	1831	0	0	0	1235	1205	1	1	1	1438	1408
0	0	0	1862	1832	0	0	0	1236	1206	1	1	1	1439	1409
0	0	0	1863	1833	0	0	0	1237	1207	1	1	1	1440	1410
0	0	0	1864	1834	0	0	0	1238	1208	1	1	1	1441	1411
0	0	0	1865	1835	0	0	0	1239	1209	1	1	1	1442	1412
0	0	0	1866	1836	0	0	0	1240	1210	1	1	1	1443	1413
0	0	0	1867	1837	0	0	0	1241	1211	1	1	1	1444	1414
0	0	0	1868	1838	0	0	0	1242	1212	1	1	1	1445	1415
0	0	0	1869	1839	0	0	0	1243	1213	1	1	1	1446	1416
0	0	0	1870	1840	0	0	0	1244	1214	1	1	1	1447	1417
0	0	0	1871	1841	0	0	0	1245	1215	1	1	1	1448	1418
0	0	0	1872	1842	0	0	0	1246	1216	1	1	1	1449	1419
0	0	0	1873	1843	0	0	0	1247	1217	1	1	1	1450	1420
0	0	0	1874	1844	0	0	0	1248	1218	1	1	1	1451	1421
0	0	0	1875	1845	0	0	0	1249	1219	1	1	1	1452	1422
0	0	0	1876	1846	0	0	0	1250	1220	1	1	1	1453	1423
0	0	0	1877	1847	0	0	0	1251	1221	1	1	1	1454	1424
0	0	0	1878	1848	0	0	0	1252	1222	1	1	1	1455	1425
0	0	0	1879	1849	0	0	0	1253	1223	1	1	1	1456	1426
0	0	0	1880	1850	0	0	0	1254	1224	1	1	1	1457	1427
0	0	0	1881	1851	0	0	0	1255	1225	1	1	1	1458	1428
0	0	0	1882	1852	0	0	0	1256	1226	1	1	1	1459	1429
0	0	0	1883	1853	0	0	0	1257	1227	1	1	1	1460	1430
0	0	0	1884	1854	0	0	0	1258	1228	1	1	1	1461	1431
0	0	0	1885	1855	0	0	0	1259	1229	1	1	1	1462	1432
0	0	0	1886	1856	0	0	0	1260	1230	1	1	1	1463	1433
0	0	0	1887	1857	0	0	0	1261	1231	1	1	1	1464	1434
0	0	0	1888	1858	0	0	0	1262	1232	1	1	1	1465	1435
0	0	0	1889	1859	0	0	0	1263	1233	1	1	1	1466	1436
0	0	0	1890	1860	0	0	0	1264	1234	1	1	1	1467	1437
0	0	0	1891	1861	0	0	0	1265	1235	1	1	1	1468	1438
0	0	0	1892	1862	0	0	0	1266	1236	1	1	1	1469	1439
0	0	0	1893	1863	0	0	0	1267	1237	1	1	1	1470	1440
0	0	0	1894	1864	0	0	0	1268	1238	1	1	1	1471	1441
0	0	0	1895	1865	0	0	0	1269	1239	1	1	1	1472	1442
0	0	0	1896	1866	0	0	0	1270	1240	1	1	1	1473	1443
0	0	0	1897	1867	0	0	0	1271	1241	1	1	1	1474	1444
0	0	0	1898	1868	0	0	0	1272	1242	1	1	1	1475	1445
0	0	0	1899	1869	0	0	0	1273	1243	1	1	1	1476	1446
0	0	0	1900	1870	0	0	0	1274	1244	1	1	1	1477	1447
0	0	0	1901	1871	0	0	0	1275	1245	1	1	1	1478	1448
0	0	0	1902	1872	0	0	0	1276	1246	1	1	1	1479	1449
0	0	0	1903	1873	0	0	0	1277	1247	1	1	1	1480	1450
0	0	0	1904	1874	0	0	0	1278	1248	1	1	1	1481	1451
0	0	0	1905	1875	0	0	0	1279	1249	1	1	1	1482	1452
0	0	0	1906	1876	0	0	0	1280	1250	1	1	1	1483	1453
0	0	0	1907	1877	0	0	0	1281	1251	1	1	1	1484	1454
0	0	0	1908	1878	0	0	0	1282	1252	1	1	1	1485	1455
0	0	0	1909	1879	0	0	0	1283	1253	1	1	1	1486	1456
0	0	0	1910	1880	0	0	0	1284	1254	1	1	1	1487	1457
0	0	0	1911	1881	0	0	0	1285	1255	1	1	1	1488	1458
0	0	0	1912	1882	0	0	0	1286	1256	1	1	1	1489	1459
0	0	0	1913	1883	0	0	0	1287	1257	1	1	1	1490	1460
0	0	0	1914	1884	0	0	0	1288	1258	1	1	1	1491	1461
0	0	0	1915	1885	0	0	0	1289	1259	1	1	1	1492	1462
0	0	0	1916	1886	0	0	0	1290	1260	1	1	1	1493	1463
0	0	0	1917	1887	0	0	0	1291	1261	1	1	1	1494	1464
0	0	0	1918	1888	0	0	0	1292	1262	1	1	1	1495	1465
0	0	0	1919	1889	0	0	0	1293	1263	1	1	1	1496	1466
0	0	0	1920	1890	0	0	0	1294	1264	1	1	1	1497	1467
0	0	0	1921	1891	0	0	0	1295	1265	1	1	1	1498	1468
0	0	0	1922	1892	0	0	0	1296	1266	1	1	1	1499	1469
0	0	0	1923	1893	0	0	0	1297	1267	1	1	1	1500	1470
0	0	0	1924	1894	0	0	0	1298	1268	1	1	1	1501	1471
0	0	0	1925	1895	0	0	0	1299	1269	1	1	1	1502	1472
0	0	0	1926	1896	0	0	0	1300	1270	1	1	1	1503	1473
0	0	0	1927	1897	0	0	0	1301	1271	1	1	1	1504	1474
0	0	0	1928	1898	0	0	0	1302	1272	1	1	1	1505	1475
0	0	0	1929	1899	0	0								

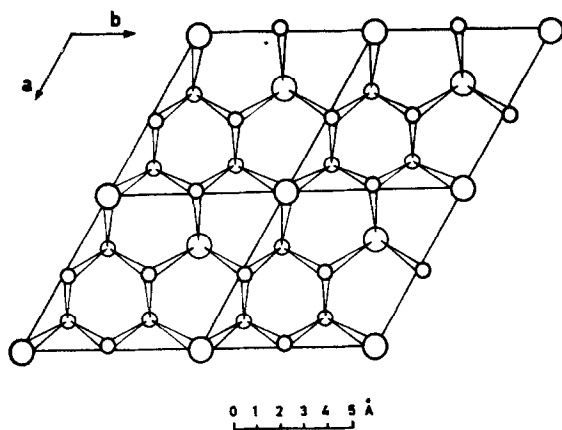


FIG. 1. The atomic arrangement in a puckered layer of SnP_3 . Small circles represent phosphorus atoms and large circles represent tin atoms.

phosphides. In a purely formalistic way polyphosphides were considered to be formed through a partial breaking down of the phosphorus network in elementary phosphorus. The metal atoms donate electrons to the phosphorus atoms, thus creating unshared electron pairs on the phosphorus atoms instead of electron pairs shared between them. These unshared pairs can then be used in bonding with the metal atoms. By considering the number and type of the different crystallographic positions occupied by phosphorus in a particular structure, it is possible to calculate an average value, N_p , for the number of phosphorus neighbors per phosphorus atom in the structure. Since this number is 3 for elementary phosphorus and it was shown (7) to be always less than 3 in polyphosphides, $(3 - N_p)$ gives the number of P-P bonds which have to be broken per phosphorus atom to form the phosphorus network in the polyphosphide. In order to retain an electron octet on phosphorus, two electrons must be supplied to the phosphorus atoms for each severed P-P bond:



i.e., one electron per atom or, if $(3 - N_p)$ bonds are broken per atom, $(3 - N_p)$ electrons per atom. If X_p denotes the number of phosphorus atoms in a formula unit, $X_p(3 - N_p)$ is the number of electrons that have to be supplied to the phosphorus network per formula unit. If there are no metal-metal bonds in the structure, the average oxidation number for the metal atoms is then given by: $(X_p/X_{\text{Me}})(3 - N_p)$, where X_{Me} is the number of metal atoms per formula unit.

In the case of SnP_3 the application of this rule is particularly simple since there is only one crystallographic position for the phosphorus atoms, each atom having two phosphorus neighbors.

By inserting the appropriate values $X_p = 3$, $X_{\text{Sn}} = 1$ and $N_p = 2$ in the formula, an oxidation number of 3 is obtained for tin in SnP_3 . Although an oxidation number which deviates from the group number is not unique for nontransition metal polyphosphides (7, 8), a value of 3 for tin is quite unexpected. Since there is only one crystallographic position for the tin atoms in SnP_3 , it would seem hardly likely that the unusual oxidation number 3 results from the simultaneous existence of tin atoms having the more usual oxidation numbers 2 and 4 in equal proportions. However, the oxidation number 3 appears more reasonable on considering the part played by tin in the structure. It has been pointed out above that the SnP_3 structure type is related to the A7, arsenic-type structure. By systematically replacing every fourth atom in an arsenic layer by tin and the rest by phosphorus, the SnP_3 structure is obtained. That is to say, tin plays structurally the same rôle as phosphorus, and in order to explain the A7-type structure, every atom has to contribute three electrons to the covalent bonding system. A similar situation seems to occur in the cubic and tetragonal high-pressure forms of SnP (10) and oxidation number 3 for germanium has been proposed for the tetragonal high-pressure forms of GeP and GeAs (6).

If the interpretation of the SnP_3 structure type given above is accepted, the fourth valence electron from tin still remains to be accounted for. It seems probable that this electron, instead of being localized on the tin atoms, goes into a conduction band. There are as yet no reliable data available on the electrical conductivity of SnP_3 , but for the isostructural GeP_3 resistivity measurements indicate metallic conductivity (6). The physical properties of SnP_3 are presently the subject of studies by resistivity, magnetic susceptibility and Mössbauer spectroscopic measurements, and the results will be reported later.

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