ACTA CHEMICA SCANDINAVICA 24 (1970) 1153–1162

# X-Ray Investigations of the Tin-Phosphorus System

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The Sn-P system has been studied by X-ray powder techniques. Three intermediate phases have been found *viz.* $Sn_4P_3$, $Sn_{0.7}P$, and $Sn_{0.3}P$. The structure of $Sn_4P_3$ has been determined using X-ray single crystal methods. The space group is $R\bar{3}m$ and the dimensions of the hexagonal unit cell are $a=3.968$ Å and $c=35.33$ Å. $Sn_4P_3$ is isostructural with $Sn_4As_3$ and the ordered form of $V_4C_3$.

The exact composition of $Sn_{0.7}P$ and $Sn_{0.3}P$ is not yet known. The powder patterns can be interpreted on the basis of hexagonal unit cells with the following dimensions:

| | | |
|---|---|---|
| $Sn_{0.7}P$ | $a=4.433$ Å | $c=28.39$ Å |
| $Sn_{0.3}P$ | $a=7.364$ Å | $c=10.528$ Å |

In a recent report by the present author [1] X-ray powder data for $Sn_4P_3$ were given together with preliminary results from a single-crystal structure determination. Since then Eckerlin and Kischio [2] have independently determined and refined the crystal structure of $Sn_4P_3$. Their results from the structure determination are in close agreement with those already given [1] and with those to be presented here; however, they claim that the composition of their crystals was $Sn_4P_{2.65}$, thus deviating considerably from the stoichiometric composition.

Arguments will be presented here to show that the composition of this phase actually is close to the ideal crystallographic formula $Sn_4P_3$. In addition the results from the refinement of the crystal structure of $Sn_4P_3$ and some comments on the existence of other intermediate phases in the Sn-P system will be given.

## EXPERIMENTAL

*Preparation.* The starting materials for the preparations were tin rods (Johnson, Matthey & Co., Ltd, spectrographically standardised, containing in ppm: Pb 5, Bi 2, Ca and Cu both<1) and red phosphorus (purity higher than 99 %). Before use the tin rods were cut into small pieces. The syntheses were as a rule performed in two steps. The first step involved the heating of weighed amounts of tin and phosphorus in evacuated and sealed silica tubes at 400°C for one week. The inhomogeneous reaction product so obtained was crushed to a fine powder and pressed into pellet form. In the second step the pellet was reheated in an evacuated silica tube at different temperatures for another

week followed by quenching or slow cooling. This procedure was undertaken in order to obtain products with high homogeneity.

*X-Ray work.* Phase-analyses of the reaction products were carried out by X-ray powder methods using Guinier-Hägg-type focussing cameras with $CuK\alpha_1$ or $CuK\alpha$ radiation. Silicon ($a=5.43054$ Å) was used as an internal calibration standard.

The single crystal investigation was performed with the equi-inclination Weissenberg method using zirconium-filtered Mo$K$ radiation and the multiple film technique with thin iron foils interleaved between successive films. The intensities were estimated visually by comparison with a calibrated intensity scale. The intensities were corrected for the Lorentz and polarisation factors as well as for absorption. In the last type of correction the outer form of the rather irregular crystal was approximated with seven boundary planes. The linear absorption coefficient, $\mu$, was taken to be equal to 160 $cm^{-1}$.

*Computing methods.* All the calculations were carried out on an electronic digital computer CD3600 using the following programs:

| | |
|---|---|
| Least squares refinement of united cell dimensions | CELSIUS: J. Tegenfeldt, Uppsala Sweden. |
| Lorentz-polarisation factor correction. Fourier summations and structure factor calculations | DRF: A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. |
| Absorption correction | DATAP2: P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson and M. Elfström, Uppsala, Sweden. |
| Least squares refinement of positional parameters, temperature factors, scale factors and degree of occupancy. | ORFLS: W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge, U.S.A.; modified by B. Sellberg, Uppsala, Sweden. |
| Interatomic distances | DISTAN: A. Zalkin, Berkeley, U.S.A. |

Atomic scattering factors and the real part of the anomalous dispersion correction were taken from tables given in *International Tables for X-ray Crystallography.*[3]

*Chemical analysis.* Since any reliable method for analysing alloys containing both tin and phosphorus does not seem to exist, the method used in the present investigation will be described in some detail. This method was developed at the Analytical Department of this institute by Dr. L. Gustafsson and Prof. F. Nydahl.

The finely ground sample was weighed into a round-bottomed flask, which was connected *via* a condenser to four washing-bottles, each containing 90 ml 0.4 % potassium permanganate and 10 ml concentrated nitric acid. The apparatus was freed from oxygen by flushing with a stream of carbon dioxide, 30 ml hydrochloric acid (1:1) previously freed from oxygen was added, and the solution was gently boiled for 1 1/2 h. To completely transfer the evolved phosphine gas to the absorption bottles, the stream of carbon dioxide was continued for another hour. In the round-bottomed flask a yellow solid which was thought to be polymeric phosphorus hydride appeared. It was filtered off and analysed for both tin and phosphorus. No tin was found in it.

The determination of phosphorus was made in two different ways depending on the amount to be determined. The combined solution from the three washing-bottles nearest to the condenser was boiled for 1/2 h in order to obtain complete oxidation to orthophosphoric acid, which was determined by precipitation as ammonium molybdophosphate and weighing as $P_2O_5 \cdot 24\ MoO_3$ according to Nydahl.[4] About 90 % of the total amount was found here. The rest of the phosphorus was found in the fourth washing-bottle (~0.4 %), in the yellow solid (~7 %) and left in the hydrochloric acid (~3 %). In the three last determinations use was made of a colorimetric method worked out at this institute (by L. Gustafsson) specially adapted for determining small amounts of phosphorus.

Tin was determined by a modified version of the method described by Farnsworth and Pekola.[5] After treatment with potassium permanganate in order to oxidize phosphorus compounds remaining in the tin solution, reduction was performed by gentle boiling with iron powder and nickel coils. The solution was cooled to about 5°C and then titrated

with a solution of potassium iodate previously standardized against a solution prepared from spectrographically pure tin rods. During the whole procedure (reduction, cooling and titration) the solution was protected from oxygen by a stream of carbon dioxide.

## PHASE-ANALYTICAL INVESTIGATIONS

By using X-ray powder methods three intermediate phases have been found *viz.* $Sn_4P_3$, $Sn_{0.7}P$, and $Sn_{0.3}P$. The exact composition of the latter two phases is not yet known. In the preliminary report [1] it was stated that there were indications of the existence of the phase SnP which previously had been described by Katz *et al.*[6] This statement was based on the appearance in one powder photogram of some weak lines at $\theta$-values close to the strongest lines reported for SnP. This observation was made on a sample with the nominal composition SnP which had been slowly cooled from about 450°C. However, despite several experiments involving slow cooling or quenching from different temperatures between 500°C and 300°C it has not been possible to re-prepare this phase.*

*β-Sn.* The observed cell dimensions for β-tin when in equilibrium with $Sn_4P_3$ at 450°C are the same within the limits of experimental error as those for pure β-tin, indicating that the amount of phosphorus taken up in solid solution is very small.

*$Sn_4P_3$.* Judging from X-ray powder photograms this phase seems to exist at the stoichiometric composition with a very small homogeneity range. No variation in the cell dimensions could be observed when comparing photograms of two phase samples quenched from 450°C on each side of the $Sn_4P_3$-composition. The single crystal investigation to be described later in this paper gave no reason to suspect any marked deviation from stoichiometry since this should have been reflected in the individual temperature factors obtained from the least squares refinement. However, from chemical analyses, Eckerlin and Kischio [2] concluded that the composition should be $Sn_4P_{2.65}$, at least for the metal-rich limit, since they prepared their crystals in a large excess of tin. As this observation seemed to be in contradiction with the results obtained in the present work it was decided to combine chemical analysis with X-ray powder analysis. Moreover, Eckerlin and Kischio determined the tin content only and then calculated the phosphorus content by difference, which is a less satisfactory procedure.

A sample with the nominal composition $Sn_4P_{2.93}$ was then prepared by repeated heat treatments and crushings, and finally quenching from 450°C. X-Ray powder photograms revealed the presence of $Sn_4P_3$ and small amounts of β-Sn. The chemical analysis gave the results: 83.46 % tin and 16.07 % phosphorus which are mean values from two determinations and correspond to the composition $Sn_4P_{2.952}$. However, the tin and phosphorus content sums up to 99.53 % only and consequently there remains about 0.5 % to take into consideration. This impurity most probably being oxygen can either be dissolved in the tin phosphide or exist as an oxide or as a phosphate. Irrespective of which alternative may be the correct one it seems impossible

* *Note added in proof.* Two high pressure forms of SnP have recently been published by Donohue.[18]

to get the composition of the phosphide even in the neighbourhood of that suggested by Eckerlin and Kischio.[2] As they prepared their crystals by slow cooling from 600°C one could then argue that their crystals correspond to another equilibrium temperature and that the very small homogeneity range observed at 450°C is considerably widened at higher temperatures. However, this should then give rise to very different cell dimensions, but as can be seen in Table 1 this is not the case.

*Table 1.* Unit cell dimensions for $Sn_4P_3$, $Sn_{0.7}P$, and $Sn_{0.3}P$. The limits of error given for cell dimensions determined in this work are standard deviations as obtained from least squares refinements.

| Compound | Hexagonal cell | | | Rhombohedral cell | | Ref. |
|---|---|---|---|---|---|---|
| | $a$ (Å) | $c$ (Å) | $c/a$ | $a$ (Å) | $\alpha°$ | |
| $Sn_4P_3$ | 3.968 ±1 | 35.34 ±1 | 8.906 | 12.001 ±3 | 19.03 ±1 | 2 |
| $Sn_4P_3$ | 3.9677±3 | 35.331±4 | 8.905 | 11.998 ±1 | 19.036±3 | this work |
| $Sn_{0.7}P$ | 4.4330±4 | 28.394±5 | 6.405 | 9.805 ±1 | 26.132±4 | » |
| $Sn_{0.3}P$ | 7.3642±6 | 10.528±1 | 1.430 | 5.5130±6 | 83.81 ±2 | » |

This combination of X-ray powder analysis and chemical analysis then makes it highly probable that the $Sn_4P_3$ phase actually exists close to the stoichiometric composition with a very small homogeneity range at 450°C.

In the single crystal investigations Eckerlin and Kischio used $Sn_4P_3$-crystals obtained from two phase samples the other phase being tin, while the present author used $Sn_4P_3$-crystals from a two phase sample on the phosphorus rich side. Consequently it should be possible to compare the results from these two investigations concerning the composition of the crystals used and to see how this fits with the chemical analysis already discussed. Using the structure factors given by Eckerlin and Kischio,[2] a least squares refinement was then started in which one scale factor, three positional parameters, one over-all temperature factor and three parameters defining the degree of occupancy for three atom positions were refined. The occupancy for one tin atom position was kept constant in order to avoid a singular matrix. The result from this refinement is collected in Table 2 together with the result from the corresponding refinement using the structure factors obtained in this work.

The method of refining the occupancy of atomic positions is not very sensitive and suffers from certain limitations. For instance, if different atoms of the same kind have very different surroundings it would give rise to different temperature factors, and this temperature factor effect is very strongly correlated to the degree of occupancy. Moreover, errors in the absorption correction or extinction effects may also influence the result. However, comparing results from two different crystals of the same phase must be considered as a favourable case as the temperature factor effect is eliminated. It must also be stressed that the occupancies obtained are on a relative scale only and can not directly be related to density measurements.

*Table 2.* Results from least squares refinements of the degree of occupancy for different atomic positions in $Sn_4P_3$ and $Sn_4As_3$. For details, see the text.

| Compound | Degree of occupancy (%) | | | | Structure factors from Ref. |
|---|---|---|---|---|---|
| | $Sn_I$ | $Sn_{II}$ | $P_I$ or $As_I$ | $P_{II}$ or $As_{II}$ | |
| $Sn_4P_3$ | 100[a] | 90±1 | 96±4 | 93±6 | this work |
| $Sn_4P_3$ | 100[a] | 98±1 | 97±4 | 107±5 | 2 |
| $Sn_4As_3$ | 100[a] | 95±1 | 101±1 | 98±1 | 2 |

[a] Arbitrarily.

In order to get an idea of how large the deviations from 100 % occupancy are expected to be if the composition were to be that claimed by Eckerlin and Kischio the following can be mentioned. Assuming that the deviation from the stoichiometric composition is caused by vacancies on the sixfold phosphorus position (see description of the structure determination in the next section) one calculates the degree of occupancy of this position to be 82.5 %. If on the other hand one makes the assumption that there is a substitution of phosphorus for tin on this position the apparent degree of occupancy should be 125 %. In both cases the threefold phosphorus position is much more sensitive so even if the vacancy formation or substitution process is associated with both the sixfold and threefold positions one would expect it to be possible to detect it in this way. There is of course the possibility of a combination of both these processes in which case it could be difficult to prove any deviation from 100 % occupancy by this method, however, in view of the large difference in size between tin and phosphorus substitution seems unlikely.

As can be seen in Table 2 the result from the single crystal investigations are in close agreement with the results obtained from the phase analysis. In one case only is there a significant deviation from full occupancy and that is for the crystal from the phosphorus rich side which seems to be a little deficient in tin, however, the degree of occupancy obtained for the phosphorus positions indicate that this effect can wholly or in part be compensated for by phosphorus vacancies. In fact, by using the degrees of occupancy obtained, the calculated composition turns out to be $Sn_4P_{3.0}$.

In conclusion, the results from the X-ray single crystal investigations are almost in complete agreement with the conclusion already arrived at from chemical analysis and X-ray powder analysis.

For the purpose of comparison the result from a least squares refinement of the isostructural $Sn_4As_3$-phase is also included in Table 2. The structure factors have been taken from Eckerlin and Kischio.[2] From chemical analysis these authors obtained the composition $Sn_{3.74}As_3$ for the metal rich limit. The result from the refinement gives some support for assuming a tin deficiency in their crystals.

*$Sn_{0.7}P$ and $Sn_{0.3}P$.* In earlier literature different phosphorus rich tin phosphides have been reported. For instance, in 1920 Vivian [7] found two compounds which were called $Sn_3P_4$ and $SnP_3$. The existence of two phases with approximate compositions $Sn_{0.7}P$ and $Sn_{0.3}P$ has now been proved by X-ray powder methods. The diffraction pattern for $Sn_{0.3}P$ is given in Table 3 and for $Sn_{0.7}P$ in a coming paper by Wadsten.[8] In both cases the diffraction

*Table 3.* Powder diffraction data up to $\theta=42°$ for $Sn_{0.3}P$. Cu$K\alpha$ radiation, $\lambda=1.54178$ Å.

| $I_o$ | *hkl* | $\sin^2\theta_o\times10^5$ | $\sin^2\theta_c\times10^5$ | $I_o$ | *hkl* | $\sin^2\theta_o\times10^5$ | $\sin^2\theta_c\times10^5$ |
|---|---|---|---|---|---|---|---|
| vvw | 101 | 1990 | 1997 | m | 134 | 27564 | 27572 |
| st | 012 | 3598 | 3606 | — | 107 | — | 27731 |
| st | 110 | 4377 | 4383 | vvw | 321 | 28279 | 28297 |
| w | 003 | 4824 | 4825 | w | 232 | 29925 | 29905 |
| vvw | 021 | 6381 | 6381 | m | 140 | 30687 | 30683 |
| vst | 202 | 7976 | 7989 | m | 404 | 31943 | 31955 |
| — | 113 | — | 9208 | w | 027 | 32084 | 32114 |
| m | 104 | 10038 | 10039 | w | 315 | 32423 | 32397 |
| vvw | 211 | 10764 | 10764 | | 306 | | 32450 |
| m | 122 | 12373 | 12372 | — | 413 | — | 35508 |
| w | 030 | 13150 | 13150 | vw | 018 | 35783 | 35773 |
| m | 024 | 14423 | 14422 | m | 324 | 36362 | 36339 |
| — | 015 | — | 14864 | — | 217 | — | 36498 |
| st | 220 | 17523 | 17533 | — | 045 | — | 36781 |
| vvw | 303 | [a] | 17975 | st | 226 | 36835 | 36833 |
| m | 214 | 18806 | 18806 | — | 051 | — | 37063 |
| m | 205 | 19264 | 19247 | vvw | 502 | [a] | 38672 |
| — | 006 | — | 19300 | w | 330 | 39470 | 39450 |
| — | 131 | — | 19530 | w | 208 | 40179 | 40156 |
| m | 312 | 21132 | 21139 | — | 235 | — | 41164 |
| vw | 223 | 22348 | 22358 | — | 241 | — | 41447 |
| — | 125 | — | 23631 | st | 422 | 43049 | 43055 |
| m | 116 | 23692 | 23684 | — | 009 | — | 43426 |
| — | 401 | — | 23914 | — | 333 | — | 44275 |
| st | 042 | 25521 | 25522 | m | 128 | 44548 | 44539 |

[a] Too weak to be measured accurately.

patterns can be interpreted on the basis of hexagonal unit cells with the dimensions given in Table 1. On inspection of the indices obtained for the observed reflexions it is seen that they fulfill the condition $-h+k+l=3n$ which indicates that the actual symmetry is trigonal with rhombohedral lattices. The corresponding rhombohedral unit cells are also given in Table 1.

Further work is needed before the exact composition and possible occurrence of homogeneity ranges for these phases can be settled. The data given here are from two phase samples $Sn_4P_3-Sn_{0.7}P$ quenched from 450°C and $Sn_{0.3}P-P$ slowly cooled from 520°C, respectively.*

## DETERMINATION AND REFINEMENT OF THE $Sn_4P_3$ STRUCTURE

The single crystal used, though rather irregular in shape nevertheless had quite a uniform cross-section not larger than 0.07 mm, and was obtained from a sample with the nominal composition SnP which had been heat treated

* *Note added in proof.* In a recent paper by Donohue and Young[17] X-ray powder data are given for a high pressure phase with the composition $GeP_3$. The cell dimensions and intensity data given indicate that that this phase is isostructural with $Sn_{0.3}P$.

at 545°C for one week followed by slow cooling. From Weissenberg photographs it was assumed that the crystals had monoclinic symmetry and that they had been rotated round the monoclinic axis. The diffraction data was indexed and the structure solved on the basis of this symmetry; however, later it was realized that the symmetry actually is trigonal and that the crystal had been rotated round the [100] direction in the non-primitive hexagonal unit cell which will be used in the following. When transforming the indices from the monoclinic to the hexagonal system care was taken to exclude reflexions which in the higher symmetry are related to each other.

Only reflexions with $-h+k+l=3n$ were observed indicating a rhombohedral lattice, and as no conditions limiting the occurrence of special reflexions could be found the existence of any translation elements of symmetry could be excluded. As the Laue symmetry was found to be $\bar{3}m$ there are three possible space groups, *viz.*, $R32$, $R3m$ and $R\bar{3}m$. When the structure was determined on the basis of monoclinic symmetry it could be shown that all the possible vectors in Patterson space were in the sections P($U0W$) and P($U1/2W$). These two sections could be interpreted in terms of space group $C2/m$ and when transforming into the higher symmetry the new space group turned out to be $R\bar{3}m$ with 12 tin atoms in two sets of 6($c$) positions and 9 phosphorus atoms distributed on one 6($c$) position and one 3($a$) 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 which were used in a least squares refinement. The parameters refined were the atomic coordinates, individual isotropic temperature factors and two scale factors one for each of the two layer lines ($0kl$) and ($1kl$), respectively. A weighting scheme according to Cruickshank *et al.*[9] $w=1/(a+|F_o|+c|F_o|^2)$, was used with the values $a=35.0$ and $c=0.006$. The refinement converged very rapidly and was stopped when the discrepancy factor $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0.081 for the 220 observed independent $F$ values.

The final structure data of $Sn_4P_3$ are as follows:

Space group: $R\ \bar{3}m$ ($D_{3d}^5$)
Hexagonal cell: $a=3.9677\pm3$ Å; $c=35.331\pm4$ Å; $U=481.7$ Å$^3$; $Z=3$
Rhombohedral cell: $a=11.998\pm1$Å; $\alpha=19.036°\pm3$; $U=160.6$ Å$^3$; $Z=1$
Calculated density: 5.870 g cm$^{-3}$
The atoms are in the 6($c$) and 3($a$) positions with the parameter values:

| | | $x$ | $y$ | $z$ | $\sigma(z)$ | $B$ (Å$^2$) | $\sigma(B)$ (Å$^2$) |
|---|---|---|---|---|---|---|---|
| $Sn_I$ | 6($c$) | 0 | 0 | 0.13405 | 0.00006 | 0.30 | 0.03 |
| $Sn_{II}$ | 6($c$) | 0 | 0 | 0.28951 | 0.00007 | 0.62 | 0.03 |
| $P_I$ | 6($c$) | 0 | 0 | 0.4289 | 0.0002 | 0.36 | 0.11 |
| $P_{II}$ | 3($a$) | 0 | 0 | 0 | — | 0.62 | 0.17 |

Interatomic distances and bond angles are given in Table 4.

As structure factors of good quality already have been published by Eckerlin and Kischio [2] those obtained in the present work are left out; however, they can be obtained upon request from the author.

## DISCUSSION OF THE $Sn_4P_3$ STRUCTURE

$Sn_4P_3$ is isostructural with $Sn_4As_3$ the structure of which was determined by Hägg and Hybinette.[10] The structure can be interpreted as a layer structure with hexagonal tin and phosphorus layers stacked on each other perpendicular to the *c*-axis. The layers are displaced relative to each other parallel with the (001)-plane resulting in each atom having an octahedral environment consisting of three atoms belonging to the layer just below and three atoms belonging to the layer just above. In all there are twelve tin atom layers

*Table 4.* Interatomic distances (Å units) and angles with standard deviations in $Sn_4P_3$. Distances shorter than 3.8 Å listed.

| | Dist. | S.d. | | Angle | S.d. | |
|---|---|---|---|---|---|---|
| $Sn_I$ —3 $P_I$ | 2.664 | 0.004 | $Sn_I$ —$Sn_I$ —$Sn_I$ | 75.25° | 0.08° | (3) |
| 3 $Sn_I$ | 3.250 | 0.003 | $Sn_I$ —$Sn_I$ —$P_I$ | 93.38 | 0.10 | (6) |
| | | | $P_I$ —$Sn_I$ —$P_I$ | 96.27 | 0.18 | (3) |
| | | | $Sn_I$ —$Sn_I$ —$P_I$ | 165.52 | 0.16 | (3) |
| $Sn_{II}$—3 $P_{II}$ | 2.765 | 0.001 | $P_I$ —$Sn_{II}$—$P_I$ | 85.20 | 0.17 | (3) |
| 3 $P_I$ | 2.931 | 0.005 | $P_I$ —$Sn_{II}$—$P_{II}$ | 91.46 | 0.08 | (6) |
| | | | $P_{II}$ —$Sn_{II}$—$P_{II}$ | 91.70 | 0.06 | (3) |
| | | | $P_I$ —$Sn_{II}$—$P_{II}$ | 175.46 | 0.13 | (3) |
| $P_I$ —3 $Sn_I$ | 2.664 | 0.004 | $Sn_I$ —$P_I$ —$Sn_I$ | 96.27 | 0.18 | (3) |
| 3 $Sn_{II}$ | 2.931 | 0.005 | $Sn_I$ —$P_I$ —$Sn_{II}$ | 88.99 | 0.05 | (6) |
| | | | $Sn_{II}$ —$P_I$ —$Sn_{II}$ | 85.20 | 0.17 | (3) |
| | | | $Sn_I$ —$P_I$ —$Sn_{II}$ | 172.10 | 0.24 | (3) |
| $P_{II}$ —6 $Sn_{II}$ | 2.765 | 0.001 | $Sn_{II}$—$P_{II}$ —$Sn_{II}$ | 91.70 | 0.06 | (6) |
| | | | | 88.30 | 0.06 | (6) |
| | | | | 180.00 | 0.00 | (3) |

and nine phosphorus atom layers in each unit cell perpendicular to the *c*-axis, consequently, there will be tin atom layers in contact with each other on three levels in every cell. The result is that the tin atom denoted $Sn_I$ has three other tin atoms and three phosphorus atoms as nearest neighbours while the coordination octahedra around $Sn_{II}$ consist of phosphorus atoms only. The phosphorus atoms have six tin atoms as nearest neighbours. The distances are found in Table 4.

Fig. 1 shows the $11\bar{2}0$ plane. As can be seen the stacking sequence for tin atom layers is ABABCACABCBC and for phosphorus atom layers BCCABBCAAB with the tin atom double layers between two phosphorus atom layers of the same type. The same stacking sequence for metal atom layers as well as for non metal atom layers has recently been observed for the ordered form of $V_4C_3$[11,12] which accordingly can be considered as isostructural with $Sn_4P_3$. However, depending on the large difference in size between vanadium and carbon atoms, $V_4C_3$ belongs to the interstitial class of compounds with carbon atoms in octahedral holes between close packed vanadium atom layers. In $Sn_4P_3$ the layers are not close packed, the shortest Sn—Sn distance

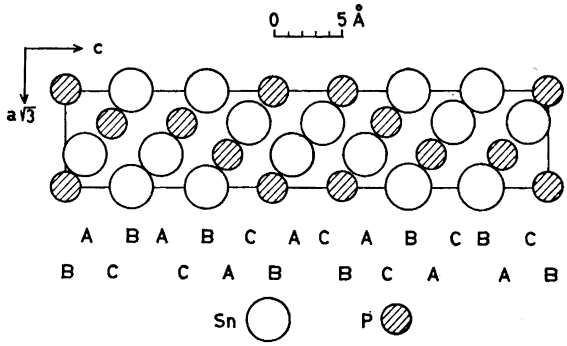


*Fig. 1.* The atomic arrangement in the $11\bar{2}0$ plane of the hexagonal unit cell in $Sn_4P_3$. The stacking sequences for tin atom and phosphorus atom layers are indicated.

within the layers being about 30 % larger than in $\beta$-tin. This indicates that the interaction between atoms belonging to the same layer must be small in $Sn_4P_3$ and that Sn – P and Sn – Sn bonds between different layers are responsible for the main part of the cohesion.

As the difference in electronegativity between tin and phosphorus is rather small the Sn – P bonds are expected to be essentially of a covalent type. Table 4 shows the coordination octahedra for $Sn_{II}$ and $P_I$ to be irregular with three neighbours somewhat closer than the three others. This may also be an indication of a directional character of the bonding. However, it is not easy to find a simple covalent model which explains both the observed coordination and the observed bonding distances. Moreover, metallic conductivity has been reported [2,13] for $Sn_4P_3$, thus making a model with filled valence orbitals unsatisfactory. At first sight it seems plausible to associate the metallic character with the Sn – Sn contacts arising when tin atom layers are stacked on each other without any interleaving phosphorus atoms. However, the conductivity was not found to be markedly anisotropic,[2] which may indicate that a model involving extensive delocalisation with bond orders less than one is better.

Geller *et al.*[14,15] have proposed an ionic model for predicting metallic behavior and for calculation of the carrier concentration in compounds related to the NaCl-type. According to this model $Sn_4P_3$ requires 3 1/2 $Sn^{2+}$ and 1/2 $Sn^{4+}$ ions with the number of charge carriers per formula unit equal to twice the number of $Sn^{4+}$ ions. This model has been questioned for $Sn_4P_3$ by van Maaren,[12] however, his arguments against the ionic model were based on the supposed deviation from the stoichiometric composition which resulted in the number of $Sn^{4+}$ ions being less than zero when assuming vacancies on the phosphorus positions. This argument is no longer valid as it has been shown in this work that $Sn_4P_3$ probably is a stoichiometric compound. However, it seems to the author that a model which takes into consideration the actual coordination, and consequently does not overlook the possibility of bonding between atoms of the same kind would be a better one.

*Acknowledgements.* I wish to thank Professor G. Hägg for all the facilities placed at my disposal and Dr. S. Rundqvist for his kind interest in this work and for much valuable advice. Thanks are also due to Professor F. Nydahl and Dr. L. Gustafsson for their great interest in the problems of chemical analysis.

The work has been financially supported by the *Swedish Natural Science Research Council.*

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Received October 9, 1969.