

An X-Ray Investigation of Transition Metal Phosphides

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The investigation reported in the following paper treats phosphides of transition metals with a low phosphorus content. The metals belong to the groups IV—VI of the periodic system, *viz.* Ti, Zr, V, Nb, Ta, Cr, Mo, W. The ratio phosphorus/metal is ≤ 1 ("subphosphides" and "monophosphides").

EXPERIMENTAL

Powdered metals of fairly high purities (about 99.5 %) and red phosphorus (Kahlbaum *pro analysi*) were used as starting materials. The phosphides were prepared by the following two methods (A and B):

A. The metal powder and red phosphorus, to a total amount of about 1 g, were mixed in various proportions, and heated in evacuated and sealed silica tubes. The heating time was varied between 1 hour and 1 month, and the temperature between 550° C and 1100° C. The best results seemed to be reached under the following reaction conditions: uniform temperature rise from room temperature up to about 800° C over a period of 2 days, heating at a constant temperature of about 800° C for about 2 days, and cooling to room temperature over a period of 1 day. Below about 650° C the rate of reaction is very slow. Above about 850° C there is a certain tendency towards reactions between the silica tube and the materials used. On account of the high vapour pressure of phosphorus at elevated temperatures, explosions are liable to take place if the silica tubes have too thin walls or are improperly sealed.

B. PH_3 , obtained from white phosphorus and potassium hydroxide solution, was dried over P_2O_5 and passed together with dry oxygen-free hydrogen over the metal powders placed in alumina boats in a porcelain-tube heated in an electric furnace. The temperatures were varied between 700° and 900° C, and the times between 2 and 10 hours. The air in the apparatus was first driven out by means of carbon dioxide, whereupon a steady stream of hydrogen was passed through. Since it proved very difficult to obtain the mono- and subphosphides in a pure state by this method, it was used for the preparation of diphosphides (800° C, 6 hours). A mixture of metal powder and diphosphides was then heated in evacuated and sealed silica tubes (method A) for the preparation of specimens with the desired compositions.

In order to homogenize the product and to detect the possible presence of high-temperature modifications of the phosphides, some samples were heated in sealed evacuated silica tubes at temperatures between 600° C and 1100° C, and then quenched in cold water.

The phase analysis and structure determinations were made from powder photographs taken with Cu-*K α* and Cr-*K α* radiation in Guinier-type cameras. The monochromator was either a curved quartz monochromator or an aluminium monochromator with double curvature¹. For measurements of the high-angle reflections additional photographs were taken with Hagg-Phragmén type focusing cameras.

THE STRUCTURES OF THE PHASES

The existence of the diphosphides of all the actual metals (Ti, Zr, V, Nb, Ta, Cr, Mo, W) was confirmed, but no attempt was made to determine the structures.

The structures and approximate compositions of all phases with the phosphorus/metal ratio close to unity were determined.

A synopsis of the phosphides' structure types, unit cell dimensions and densities, both calculated and observed, are given in Table 5. The interatomic distances are listed in Table 6.

1. The Ti—P System

According to Biltz, Rink and Wiechmann², two titanium phosphides exist, one of them being homogeneous in the interval $\text{TiP}_{0.92-0.94}$ and the other having the approximate composition Ti_2P .

The existence of a "subphosphide" was confirmed in the present work, although its structure and composition is unknown.

TiP

The powder photograph reflections of a phase which was homogeneous at the composition TiP indicated hexagonal symmetry. The observed density value, 4.08, corresponds to four formula units TiP in the unit cell. There were no reflections with $h-k = 3n$ and $l \neq 2n$ simultaneously. The space-group with the highest symmetry fulfilling these conditions is $D_{6h}^4-P6_3/mmc$ with the atoms in combinations of the positions 2(a) 0, 0, 0; 0, 0, $\frac{1}{2}$, 2(b) 0, 0, $\frac{1}{4}$; 0, 0, $\frac{3}{4}$; 2(c) $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$, 2(d) $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$, and 4(f) $\frac{1}{3}$, $\frac{2}{3}$, z ; $\frac{2}{3}$, $\frac{1}{3}$, \bar{z} ; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2} + z$; $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2} - z$ with $z = 1/8$. As is evident from Table 1 good agreement between calculated and observed intensities is obtained for the following atomic grouping:

4 Ti in 4 (g) $\frac{1}{3}$, $\frac{2}{3}$, z with $z = 1/8$,

2 P in 2 (a) 0, 0, 0; 0, 0, $\frac{1}{2}$,

2 P in 2 (d) $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$

If the projections of the positions on the basal plane are designated by A, B, and C, the titanium lattice can be symbolized by the sequence AABBAABB . . . The corresponding phosphorus atom sequence is ACBCACBC . . ., a mixture of cubic and hexagonal close-packing. The resulting stacking of atoms is $A_{Ti}B_{PA}A_{Ti}C_{PB}A_{Ti}B_{TC}P$. . .

The phosphorus atoms are thus placed at the centres of metal atom octahedra. The lattice can be considered as a superstructure of the NiAs (B 8) lattice. The same arrangement of metal atoms occurs in MoC (γ' -phase)³, NbN (I)⁴, W_2B_5 ⁵ and Ti_2B_5 ⁶. In the boride phases the parameter z is slightly differed from 1/8. From space considerations, the nonmetal atoms in MoC (γ') and NbN (I) ought to be placed in the same positions as the phosphorus atoms in TiP. These three compounds are therefore probably isomorphous. The atomic arrangement gives an explanation of the fact that the parameter z does not differ from the value 1/8. The "anti-form" of the TiP structure has recently been found for the ternary nitride Ta_3MnN_4 ⁷.

Table 1. Calculated and observed intensities for the TiP phase.

hkl	I_{calc}	I_{obs}	hkl	I_{calc}	I_{obs}
0,0,2	0	0	2,0,8	71	80
1,0,0	41	35	2,1,5	83	80
1,0,1	83	75	3,0,0	15	10
0,0,4	8	10	1,0,11	37	35
1,0,2	108	115	3,0,2	0	0
1,0,3	231	250	2,1,6	23	25
1,0,4	96	80	2,0,9	5	0
0,0,6	0	0	0,0,12	1	0
1,0,5	127	115	1,1,10	0	0
1,1,0	176	175	3,0,4	5	0
1,1,2	0	0	2,1,7	11	10
1,0,6	28	25	1,0,12	16	10
2,0,0	6	5	2,0,10	7	0
2,0,1	14	35	2,1,8	10	10
1,1,4	19		3,0,6	0	0
2,0,2	21	25	2,2,0	43	35
1,0,7	14	50	2,0,11	25	25
0,0,8	46		2,2,2	0	0
2,0,3	81	80	1,0,13	27	25
2,0,4	40	25	2,1,9	7	0
1,0,8	11	10	1,1,12	5	0
1,1,6	0	0	3,1,0	5	0
2,0,5	62	50	3,1,1	8	10
2,0,6	17	15	2,2,4	5	
1,0,9	74	75	0,0,14	0	0
0,0,10	0	0	3,1,2	18	15
2,1,0	71	75	3,0,8	111	115
2,1,1	14	10	3,1,3	71	80
2,1,2	23	25	2,0,12	21	15
2,0,7	71	75	2,1,10	22	15
1,1,8	147	175	3,1,4	51	50
2,1,3	83	80	1,0,14	14	15
1,0,10	21	10	2,2,6	0	0
2,1,4	49	50			

2. The Zr—P system

Strotzer, Biltz, and Meisel⁸ reported three intermediate phases, *viz.* Zr_3P , ZrP , and ZrP_2 .

The present work confirmed the existence of a phosphide of unknown composition and structure within the interval $ZrP_{0.3-0.5}$.

 α -ZrP

In the vicinity of the composition $ZrP_{0.3}$, a phosphide occurred which had a comparatively small homogeneity range. The phase is of NaCl type, and the length of the cube edge was found to vary between 5.261 Å and 5.278 Å. The zinc blende structure (B 3 type) could be rejected, both because of disagreement between calculated and observed intensities and from space considerations.

Table 2. Calculated and observed intensities for the VP phase assuming, I: "Anti-NiAs" structure, or II: NiAs structure.

<i>hkl</i>	<i>I_{calc}</i>		<i>I_{obs}</i>
	I	II	
0,0,2	6	6	5
1,0,0	1	35	35
1,0,1	84	29	25
1,0,2	74	101	100
1,0,3	28	8	10
1,1,0	44	44	50

The NaCl structure gives ZrP as the ideal formula for this phase. A small fraction of the P positions is evidently empty. It therefore seems practical to call the phase ZrP and to denote it by α -ZrP in order to distinguish it from the following phase.

β -ZrP

This phase appeared to be homogeneous at the composition ZrP, and is isomorphous with the TiP phase.

3. The V—P system

The vanadium-phosphorus system was examined by Zumbusch and Biltz⁹. Their investigation indicated the existence of the compounds V₃P, VP and VP₂. The formula V₂P was given for the subphosphide by Chêne^{10,11} and Andrieux¹².

Powder photographs of samples with the compositions VP_{0.2}, VP_{0.4}, VP_{0.6}, VP_{0.8}, VP_{1.0}, and VP_{1.2} showed that the only compound existing in the V—VP interval is the VP phase.

From Table 2 is evident that VP has the NiAs structure (B 8 type). The space-group is thus D_{6h}^4 — $P6_3/mmc$ with 2 V in 2(*a*) 0, 0, 0; 0, 0, $\frac{1}{2}$ and 2 P in 2(*c*) $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$. The homogeneity range is small. The *c/a* value is remarkably high: 1.96. For other crystals with well established NiAs structure *c/a* has been found to range between 1.2 and 1.7. The VP phase seems to be the only existing phosphide of B 8 type.

4. The Nb—P and Ta—P systems

According to Zumbusch and Biltz^{13,14}, the niobium and tantalum phosphides are probably isomorphous. They point out that the monophosphides occur in two modifications, none of them related to the vanadium monophosphide, and that the diphosphides give a diffraction pattern similar to that of the vanadium diphosphide.

The present work confirmed the results given by these authors.

α -NbP

A homogeneous phase was obtained at the approximate composition NbP_{0.95}. The powder pattern of this phase corresponds to a body-centered tetragonal cell containing one unit NbP_{0.95}. In order to facilitate the comparison

with the following phase the corresponding face-centered cell containing two units $\text{NbP}_{0.95}$ has been chosen here.

Consequently, the atoms are distributed over the positions $0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$. As compared with the cubic close-packing ($c/a = 1$), the tetragonal deformation is very strong, $c/a = 1.71$. The lattice can be considered to be built up of two-dimensional layers parallel to $(0, 0, 1)$. The strong bonds exist within each NbP layer and only comparatively weak bonds between the layers. Since the interatomic distance in a layer reaches the remarkably low value of 2.35 Å (4-coordination), the only possible atomic arrangement is a partly ordered grouping. Within a layer each Nb atom is always surrounded by four P atoms. For it is most unlikely that the Nb—Nb distances are less than 2.6 Å, and the observed P—P distances of all the examined phosphides exceed the value of 3.1 Å. But it is evident from the diffraction pattern (no lines with mixed indices are visible) that the NbP layers are irregularly displaced in relation to each other. The atomic distribution in the unit cell can therefore be written as: 1 Nb + 1 P in $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0$ and 1 Nb + 1 P in $0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}$, with ordered positions of the atoms within each 001-plane.

$\beta\text{-NbP}$

This phase was found to be homogeneous at the composition 1 : 1. Besides the strong diffraction lines characteristic for the face-centered arrangement of atoms, the powder photograph showed a series of extra reflections from a tetragonal lattice having the value of the c -axis twice that of the $\alpha\text{-NbP}$ phase. Reflections with $h + k + l = 2n$, $h00$ with $h = 2n, 0, 0$, l with $l = 4n, 2h + l = 2n + 1$ or $4n$ appeared in the photographs. This is characteristic for the space-group C_4^6-I4 and $D_4^{10}-I4_12$. According to the density determinations, the unit cell contains 4 Nb and 4 P atoms. The only possible atomic position in the space-group C_4^6-I4 is $4(a) (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + 0, 0, z; 0, \frac{1}{2}, \frac{1}{4} + z$. Both the metal and nonmetal atoms have to be placed in this position. From $p|F|^2$ calculations it was found that $|z_{\text{Nb}} - z_{\text{P}}| = \frac{1}{2}$, meaning a fourfold screw-axis 4_1 (or 4_3) in the $|0, 0, 1|$ -direction. The space group is thus $D_4^{10}-I4_12$ with 4 Nb in $4(a) (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + 0, 0, 0; 0, \frac{1}{2}, \frac{1}{4}$ and 4 P in $4(b) (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + 0, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{3}{4}$.

While the NbP layers of the $\alpha\text{-NbP}$ phase occupy disordered positions in relation to each other, the $\beta\text{-NbP}$ lattice has an ordered atomic arrangement.

Intensities for the $\beta\text{-NbP}$ phase, both calculated and observed, are compared in Table 3.

$\alpha\text{-TaP}$

$\alpha\text{-TaP}$ is isomorphous with $\alpha\text{-NbP}$, and probably has the corresponding approximate composition $\text{TaP}_{0.95}$. It was not possible to obtain this phase in a pure state.

$\beta\text{-TaP}$

The $\beta\text{-TaP}$ phase is isomorphous with $\beta\text{-NbP}$, and was found to be homogeneous at the composition 1 : 1.

Table 3. Calculated and observed intensities for the β -NbP phase.

<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}	<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}
1,0,1	51	40	1,1,10	28	25
0,0,4	65	85	2,0,9	4	0
1,0,3	26	25	3,0,5	4	0
1,1,2	117	125	1,0,11	3	0
1,0,5	12	10	2,1,9	6	0
2,0,0	31	40	0,0,12	5	5
1,1,6	52	60	3,1,6	39	40
2,1,1	17		3,2,1	6	
1,0,7	8	5	3,0,7	3	0
2,0,4	52	60	2,2,8	18	15
0,0,8	13	15	3,2,3	6	0
2,1,3	6	5	3,2,5	6	0
2,1,5	12	10	2,1,11	5	0
1,0,9	5	5	1,0,13	3	0
2,2,0	16	25	3,0,9	3	0
3,0,1	6	5	4,0,0	10	10
2,1,7	9	5	4,1,1	9	10
2,2,4	28	25	3,2,7	9	10
2,0,8	28	25	4,0,4	34	40
3,0,3	4	0	4,1,3	10	10
3,1,2	56	60			

5. The Cr—P system

The existence of the Cr₃P and CrP phases was proved by Nowotny and Henglein¹⁵ by X-ray methods. Cr₃P is isomorphous with Mn₃P¹⁶, Fe₃P^{17,18}, Ni₃P¹³ and (Fe, Ni)₃P²⁰ with the atoms in the probable space-group $S_4^2-I_4^{18,21}$. CrP is of the B 31 type²², isomorphous with MnP, FeP, and CoP²³.

CrP

The CrP phase has 4 Cr and 4 P atoms in the positions $4(c) \pm (x, y, \frac{1}{4}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4})$ in the space-group $D_{2h}^{16}-Pbnm$. Nowotny and Henglein reported the same parameter values for CrP as was earlier given for MnP²³, *i.e.* $x_{Cr} = 0.20$; $y_{Cr} = 0.005$; $x_P = 0.57$; $y_P = 0.19$. The present author, however, found the best agreement between calculated and observed intensities for the following values: $x_{Cr} = 0.16$; $y_{Cr} = 0.00$; $x_P = 0.63$; $y_P = 0.20$.

The B 31 type (MnP structure) can be regarded as an orthorhombic deformed B 8 type (NiAs structure). Though the NiAs structure is hexagonal, it may be described as an arrangement with the symmetry of D_{2h}^{16} in the special case of the axial ratio $\sqrt{3} : b/c : 1$ and the atoms located in two four-fold positions $4(c) x, y, \frac{1}{4}$, with the parameters for the metal atoms $x = 0.25$; $y = 0$ and for the phosphorus atoms $x = 0.58$; $y = 0.25$. As is evident from the parameter values given above, those obtained in the present investigation signify a comparatively large deviation from the "ideal" atomic positions.

But on the other hand, the resulting interatomic distances are in good agreement with analogous distances observed for the monophosphides of the other transition metals studied here (Table 6).

6. The Mo—P system

The phases Mo_3P and MoP were reported by Andrieux and Chêne^{12,24} and according to Faller and Biltz²⁵ Mo_3P is isomorphous with Cr_3P ¹⁵.

MoP

The MoP phase was found to have the WC structure. Very small variations of the lattice constants were measured, and the formula was found to correspond to the composition 1 : 1. No extra reflections appeared in the powder photographs. This excludes an arrangement of the P atoms corresponding to the NiAs type.

7. The W—P system

Whereas the formula W_4P and W_2P were given for the tungsten subphosphides by Hartmann and Orban²⁶, Faller and Biltz²⁷ showed that W_2P is a mixture of W and WP of MnP type. But the latter authors did not publish any parameter values. They further pointed out that WP_2 is isomorphous with MoP_2 , but not with CrP_2 .

The present author found that powder photographs of samples with the compositions $\text{WP}_{0.2}$, $\text{WP}_{0.4}$, $\text{WP}_{0.6}$, and $\text{WP}_{0.8}$, only showed diffraction lines of the W and WP phases, confirming the results obtained by Faller and Biltz²⁷.

WP

As [pointed out above, no unit cell dimensions or parameter values for the atomic positions have hitherto been given for the WP phase. In the diffraction pattern there appeared $0kl$ reflections with $k = 2n$ and $h0l$ reflections with $h + l = 2n$, characteristic for the space-group D_{2h}^{16} — $Pbnm$ (compare the isomorphous CrP phase). The lines, which did not fulfill the conditions: $h + k + l = 2n$, $0kl$ with $k = 2n$ and $l = 2n$, were found to be very weak and only appeared at relatively small diffraction angles. It was therefore assumed that the phosphorus gave rise to these weak reflections. This gives $y_w = 0$. A systematic variation of x_w within the limits of closest approach between the tungsten atoms (about 2.6 Å) resulted in a value of $x_w = 0.175$ for the best agreement between calculated and observed intensities. Because of the great difference between the atomic factors of tungsten and phosphorus, it is very difficult to determine the position of the nonmetal atoms by means of X-ray data. The parameters x and y for the phosphorus atoms have thus been determined with a view to the best space distributions $x_P = 0.62$ and $y_P = 0.20$.

WP thus has 4 W and 4 P atoms located in two four-fold positions $4(c) \pm (x, y, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2})$ in the space-group D_{2h}^{16} — $Pbnm$, with the following parameter values: $x_w = 0.175$; $y_w = 0$; $x_P = 0.62$; $y_P = 0.20$.

Calculated and observed intensities are compared in Table 4.

Table 4. Calculated and observed intensities for the WP phase.

<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}	<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}
1,0,1	125	75	0,2,4	7	5
0,0,2	56	75	4,1,3	2	0
0,1,1	182	175	1,2,4	0	0
2,0,0	103	110	2,1,5	36	35
1,0,2	4	5	5,0,2	0	0
2,0,1	1	5	4,2,0	36	35
1,1,1	6	5	0,3,1	28	35
2,1,0	1	5	5,1,1	0	0
2,0,2	39	40	3,2,3	67	70
1,1,2	175	175	4,2,1	0	0
2,1,1	211	175	4,0,4	4	0
1,0,3	94	110	1,3,1	0	0
3,0,1	25	25	2,2,4	7	5
2,1,2	0	0	3,0,5	17	15
0,1,3	7	10	0,0,6	16	15
2,0,3	0	0	1,0,6	0	0
1,1,3	1	0	5,1,2	43	35
3,0,2	0	0	4,2,2	22	25
0,2,0	46	50	2,3,0	0	0
3,1,1	1	0	1,3,2	43	35
0,0,4	6	5	5,0,3	31	35
1,2,1	22	25	4,1,4	0	0
1,0,4	0	0	2,3,1	50	50
2,1,3	0	0	3,1,5	0	0
3,1,2	61	50	2,0,6	28	
0,2,2	21	25	1,1,6	58	110
4,0,0	35	35	1,2,5	30	
2,2,0	48	50	3,2,4	0	0
3,0,3	67	75	2,3,2	0	0
1,2,2	2	5	0,3,3	1	0
4,0,1	0	0	5,1,3	0	0
2,2,1	0	0	6,0,0	13	10
2,0,4	3	0	4,2,3	0	0
1,1,4	102	110	1,3,3	0	0
4,1,0	1	0	6,0,1	0	0
4,0,2	19	15	4,0,5	0	0
3,1,3	0	0	2,1,6	0	0
2,2,2	36	35	2,2,5	0	0
4,1,1	73	75	3,3,1	0	0
2,1,4	1	0	5,2,1	11	10
1,2,3	90	110	5,0,4	0	0
1,0,5	27	25	6,1,0	0	0
3,2,1	28	25	6,0,2	8	10
4,1,2	0	0	3,0,6	0	0
3,0,4	0	0	2,3,3	2	0
4,0,3	1	0	6,1,1	45	50
2,2,3	0	0	4,1,5	25	25
0,1,5	17	15	3,3,2	34	25
3,2,2	0	0	5,2,2	0	0
2,0,5	0	0	5,1,4	44	35
1,1,5	1	0	4,2,4	4	0
3,1,4	74	75	1,0,7	1	0
5,0,1	5	0	6,1,2	0	0

Table 4. *Cont.*

<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}	<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}
3,1,6	4	0	6,2,0	33	75
1,3,4	46	75	2,1,7	66	
3,2,5	26		25	0,3,5	18
0,2,6	23	0	5,1,5	0	0
6,0,3	0	0	6,1,2	0	0
1,2,6	0	0	6,0,4	3	0
4,3,0	0	0	4,1,6	0	0
0,1,7	28	25	4,2,5	0	0
3,3,3	0	0	7,0,1	7	0
4,3,1	41	50	0,4,0	20	15
5,2,3	53	50	1,3,5	0	0
2,0,7	0	0	3,0,7	2	0
1,1,7	0	0	3,3,4	80	75
2,3,4	0	0	5,2,4	0	0
5,0,5	13	10	4,3,3	5	0
4,0,6	26	25	1,4,1	19	50
6,1,3	5	0	6,2,2	35	
2,2,6	52	50	3,2,6	0	0
4,3,2	0	0	7,0,2	0	0
			6,1,4	0	0

GENERAL DISCUSSION

All the phosphides listed in Table 5 have a greyish black metallic lustre, and are not attacked by water or dilute acid at room temperature. Samples of TiP, ZrP, and VP were not oxidized or decomposed when heated in air at 1 000° C for one hour.

The highest nonmetal content of carbides and nitrides of all transition metals, with the exception of the lanthanides and actinides, is about 50 atom-%. The nonmetals are interstitially situated at the centres of octahedra or trigonal prisms of metal atoms. The metal lattice commonly forms a hexagonal or cubic close-packing, in a few cases a simple hexagonal arrangement of atoms. The interatomic metal-metal distances are up to about 10 % larger than those of the pure metals, and the corresponding coordination numbers are high, varying between 8 and 12.

Hägg^{28,29} has found empirically that the radius ratio nonmetal/metal is a determining factor for the structure of the phases and has an upper critical value of about 0.59. When the radius ratio exceeds 0.59 the structure is complicated, but the compounds are still metallic in character. This is characteristic of most borides and silicides. Space considerations account for the decrease in the coordination number of the metal atoms, but the coordination number for metal atom — nonmetal atom is still high. Furthermore, there exist "contact" bonds of non-ionic type between boron-boron and silicon-silicon atoms. Such nonmetal "contacts" have *not* been found to exist among the carbides and nitrides. For this reason, boron and silicon occurring in compounds with transition metals can be characterized as metals.

The radius value for the phosphorus atom has been found to be about 1.06 Å (Table 6). For the metals used here the radius ratio P/Me (Me = tran-

Table 5. Structures and unit cell dimensions of the phosphides of Ti, Zr, V, Nb, Ta, Cr, Mo, W and the phosphorus metal ratio ≤ 1 .

Phase	Structure type	Space-group	Z	Cell dimensions in Å (Error: $< \pm 1\%$)	Vol/metal-atom Å ³	Density	
						calc	obs
TiP		$P6_3/mmc$	4	$c=11.65, a=3.487; c/a=3.34$	30.67	4.27	4.08
α -ZrP	NaCl	$Fm\bar{3}m$	4	$a=5.27$	36.62	5.43	5.10
β -ZrP	TiP	$P6_3/mmc$	4	$c=12.52, a=3.677; c/a=3.40$	36.65	5.57	5.35
VP	NiAs	$P6_3/mmc$	2	$c=6.22, a=3.18; c/a=1.96$	27.20	5.00	4.72
α -NbP		$F4/mmm$	4	$c=5.69, a=3.32; c/a=1.71$	31.35	6.40	
β -NbP		$I4_12$	8	$c=11.38, a=3.325; c/2a=1.71$	31.46	6.54	6.15
α -TaP	α -NbP	$F4/mmm$	4	$c=5.69, a=3.320; c/a=1.71$	31.35	11.04	
β -TaP	β -NbP	$I4_12$	8	$c=11.39, a=3.330; c/2a=1.71$	31.57	11.15	10.3
Cr ₂ P	Fe ₃ P	$(I\bar{4})$	8	$c=4.567, a=9.144; c/a=0.50$	15.91	6.51	6.25
CrP	MnP	$Pbnm$	4	$a=6.108, b=5.362, c=3.113$	25.11	5.49	5.25
Mo ₃ P	Fe ₃ P	$(I\bar{4})$	8	$c=4.923, a=9.729; c/a=0.51$	19.42	9.09	8.60
MoP	WC	$P6m2$	1	$c=3.20, a=3.23; c/a=0.99$	28.64	7.50	7.20
WP	MnP	$Pbnm$	4	$a=6.219, b=5.717, c=3.238$	28.78	12.40	11.7

sition metal) exceeds the value 0.59 by between 10 and 30 %. From the structure determinations it is further evident that no P—P bonds of non-ionic type exist in the phosphides investigated in the present study. It is therefore of interest, that many of the monophosphides have structures analogous to those of the carbides and nitrides.

The metal atoms of the MoP phase form a simple hexagonal lattice. If we assume radii corresponding to neutral atoms, the available space permits another nonmetal atom to be placed in the metal lattice of the carbides and nitrides with the stacking AA . . . In this case both centres of the two trigonal metal atom prisms of the unit cell would be occupied. But as the observed phase composition is always close to the ratio 1 : 1, this case never occurs. This can be explained by an electron displacement from the metal towards the nonmetal atoms causing an increase in the radius of the latter. The corresponding bonds would then not have a pure metallic character but would be partially ionic.

The radius values for the carbon and nitrogen atoms are 0.77 Å and 0.71 Å respectively. Because of the comparatively large value for the phosphorus atoms, about 1.06 Å, the metal lattice in a phosphide of "interstitial" structure must be considerably expanded compared with that of analogous carbides and nitrides. The intermetallic distances in VP are 21 % and in MoP 18 % greater than in the corresponding metals, indicating a weakening of the metal bonds. The stability of the compound must be largely due to strong metal/phosphorus bonds (6-coordination) — probably of a partial ionic nature. The interatomic P—P distances follow the variation of the atomic radii of the metals. As a consequence, the nonmetal atoms are partially or entirely isolated from each other in the lattice, both in a geometrical and in a chemical (no covalent bonds) sense. This is also the case for the metallic carbides, nitrides, and oxides.

If the simple hexagonal metal lattice is "filled" with nonmetal atoms, the so-called AlB_2 structure (C 32 type) is formed, common for several diborides³⁰: TiB_2 , ZrB_2 , HfB_2 , VB_2 , NbB_2 , TaB_2 , CrB_2 , and MoB_2 . As $r_B = 0.87$ Å

Table 6. Interatomic distances (in Å) of closest approach in the phosphides. The atomic radii of phosphorus have been calculated on the assumption of non-ionic bonds and metal coordination numbers = 8.

Phase			$r_{\text{Me}^{3+}}$ / 8-coord.	$r_{\text{P}}(\text{calc.})$
<i>TiP</i>	Ti — 1Ti 2.91 6P 2.48	P — 6Ti 2.48 6P 3.49 6P 3.54) 3.51	1.42	1.06
<i>α-ZrP</i>	Zr — 6P 2.64	P — 6Zr 2.64 12P 3.73	1.54	1.10
<i>β-ZrP</i>	Zr — 1Zr 3.13 6P 2.64	P — 6Zr 2.64 6P 3.68 6P 3.78) 3.73	1.54	1.10
<i>VP</i>	V — 6P 2.41	P — 6V 2.41 6P 3.18 6P 3.61) 3.39	1.31	1.10
<i>α-NbP</i>	Nb — 4P 2.35 (4Nb + 4P) 3.29	P — 4Nb 2.35 4P 3.32 (4P + 4Nb) 3.29	(1.43)* 1.28	1.07
<i>β-NbP</i>	Nb — 4P 2.35	P — 4Nb 2.35 4P 3.32 4P 3.30) 3.31	(1.43)* 1.28	1.07
<i>α-TaP</i>	Ta — 4P 2.35 (4Ta + 4P) 3.30	P — 4Ta 2.35 4P 3.32 (4Ta + 4P) 3.30	(1.44)* 1.30	1.05
<i>β-TaP</i>	Ta — 4P 2.36	P — 4Ta 2.36 4P 3.33 4P 3.30) 3.31	(1.44)* 1.30	1.06
<i>CrP</i>	Cr — 2Cr 2.48 2P 2.25 2P 2.27 1P 2.37	P — 2Cr 2.25 2Cr 2.27 1Cr 2.37 2P 3.08 2P 3.11) 3.10	1.26	1.02
<i>MoP</i>	Mo — 6P 2.46	P — 6Mo 2.46 2P 3.20 6P 3.23) 3.22	1.36	1.10
<i>WP</i>	W — 2W 2.71 2P 2.38 2P 2.43 1P 2.55	P — 2W 2.38 2W 2.43 1W 2.55 2P 3.18 2P 3.24) 3.21	1.37	1.06

* As the niobium and the tantalum atoms have 4-coordination in the MeP planes the radii values for this coordination number have been calculated from Pauling's correction factors³⁴, taking the Born exponent $n \sim 9$.

and $r_{\text{P}} = 1.06$ Å the metal-metal distances in the phases VB_2 ³¹ and MoB_2 ³² are shorter than in VP and MoP, but still essentially greater than in the corresponding pure metals — for the diborides VB_2 and MoB_2 the increase is 15 % and 13 % respectively. A corresponding comparison between inter-

metallic distances in MoC³ and Mo, VC³³ and V results in the values 6 % and 8 % respectively.

As has been pointed out above, TiP and β -ZrP phases are isomorphous with MoC (γ' -phase)³ and NbN (I)⁴. The stacking of the metal atoms can be symbolized by the sequence AABBAABB... The phosphorus atoms are situated in the lattice holes so that the highest possible P—P distances are attained. A calculation of the mean intermetallic distances (10-coordination) in these two compounds gives values 17 % and 14 % greater than those observed for the corresponding pure metals. The Nb—Nb distances in NbN (I) are 6 % greater than those found in niobium metal.

Two borides with the same arrangement of metal atoms as in the TiP phase have been found to exist, *viz.* W₂B₅⁵ and Ti₂B₅⁶. But in these compounds the boron atoms occupy ten lattice "holes" in the unit cell instead of four [TiP, β -ZrP, NbN (I), MoC (γ')], giving rise to hexagonal two-dimensional boron nets and slightly puckered boron nets, both with boron-boron bonds.

The structure of the NbP and TaP modifications seem to be unique, with two-dimensional metal-phosphorus layers. As metal-nonmetal bonds exist only within such layers and not between them, the separate layers must be bonded together by metallic forces. The interatomic P—P distances are so great as to isolate the phosphorus atoms from each other. The metal-metal distances both within the metal-phosphorus layers (4-coordination) and between them (4-coordination) are 15 % greater than in the pure metals.

The metal atoms in CrP, WP and isomorphous phases of the MnP structure (B 31 type)²³ are surrounded by two metal atoms at "contact" distances and six metal atoms at considerably larger distances. The structure can be regarded as a strongly deformed NiAs type, with the phosphorus atoms located at the centres of deformed metal atom octahedra. The calculated mean values of the intermetallic distances are between 15 and 20 % greater than in the corresponding pure metals.

The structures of the subphosphides of the metals Ti, Zr, Cr, and W are not known, but the symmetry, unit dimensions and cell contents are known for the Cr₃P and W₃P phases. An approximate calculation of the intermetallic distances in these compounds by means of the values obtained for unit cell values or densities of the pure metals, the subphosphides and the monophosphides, indicates a linear expansion of about 5 % (8-coordination) compared with the corresponding metals Cr and W. This corresponds to the observed value of the increase in the intermetallic distance for many metallic carbides, nitrides, and oxides. This agrees with the view that a decrease of the nonmetal content in a compound results in an increase of metallic properties. When the number of nonmetal atoms of a fixed kind is increased, or when the nonmetal atoms in a fixed composition are replaced by other nonmetal atoms with a greater atomic radius, the intermetallic distances will be enlarged and/or the metal-metal coordination number will decrease.

A continuous nonmetal-metal transition takes place in group Vb of the periodic system (N, P, As, Sb, and Bi), N being a nonmetal. As having the properties characteristic for a nonmetal as well as a metal, and Bi being a metal. Intermediate phases MeX_x of corresponding composition, containing a transition metal (Me) and any of the group Vb elements (X), must have a

minimum of metallic character when $X = \text{phosphorus}$. The strong metallic properties of the nitrides are explained by the favourable geometrical conditions for the formation of common "interstitial" compounds.

The increase in the radius of X on going from N to P results in an increase in metal-metal distances, and thus in a weakening of the metal-metal bond strength in lattices of analogous types, *i.e.* with as high coordination numbers as in the pure metals. With further increase of the radius value of $X(\text{As} \rightarrow \text{Sb} \rightarrow \text{Bi})$, it is highly probable that intermediate phases will occur with the $\text{Me}-\text{Me}$ coordination number smaller than 8. But on the other hand, the $\text{Me}-X$ bonds will show a continuous increase in metallic strength. The antimonides and bismuthides can be characterized as intermetallic compounds.

SUMMARY

The $\text{Ti}-\text{P}$, $\text{Zr}-\text{P}$, $\text{V}-\text{P}$, $\text{Nb}-\text{P}$, $\text{Ta}-\text{P}$, $\text{Cr}-\text{P}$, $\text{Mo}-\text{P}$, and $\text{W}-\text{P}$ systems have been investigated by X-ray methods for phosphorus contents up to about 50 atom-%. The structures of all monophosphides have been determined and — with the exception of NbP and TaP — have been found to be of types analogous to those of metallic carbides and nitrides.

TiP and $\beta\text{-ZrP}$ are isomorphous with MoC (γ' -phase) and NbN (I), the metal atoms being arranged in the stacking sequence AABBAABB...

$\alpha\text{-ZrP}$ ($\text{ZrP}_{0.9}$), VP , and MoP possess NaCl , NiAs , and WC structures respectively.

The phases $\text{NbP}_{\sim 0.95}$ ($\alpha\text{-NbP}$) and NbP ($\beta\text{-NbP}$) have analogous tetragonal lattices, both built up of two-dimensional NbP layers, but in the first phase these are disordered relative to each other and in the latter they occupy ordered positions. The ordering leads to a doubling of the c -axis of the unit cell.

The two TaP modifications are isomorphous with the corresponding NbP phases.

The existence of the compounds Cr_3P and Mo_3P of the Fe_3P structure type has been confirmed.

The positions of the atoms in the CrP and WP phases of the MnP structure type have been redetermined.

All the phosphides have greyish black metallic lustre and are markedly resistant to chemical reagents.

The phosphides are compared with the metallic carbides, nitrides, borides, and silicides of the transition elements in a general discussion. They can be characterized as a peripheric group of these metallic compounds, having analogous structure configurations but weaker metal-metal bonds. The metal-phosphorus bonds are strong, probably of a partial ionic nature.

The radius of the phosphorus atom has been found to have a mean value of about 1.06 Å.

The author wishes to express his gratitude to Professor G. Hägg for his encouraging interest in the present investigation. This work has been supported by a grant, which is gratefully acknowledged, from *Statens Tekniska Forskningsråd*. I also wish to thank Mrs. U. Schönberg and Mr. S. Hedling for their valuable assistance in the preparation of the samples.

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Received November 27, 1953.