Phase Relationships in the Ti—P System with some Notes on the Crystal Structures of TiP$_2$ and ZrP$_2$

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The Ti—P system has been investigated by metallographical and X-ray methods. Phase equilibria have been studied between 500°C and 2000°C.

The crystal structures of TiP$_2$ and ZrP$_2$ have been refined from X-ray powder diffraction data. Both compounds crystallize with the PbCl$_2$-type structure, the orthorhombic unit cell dimensions are for TiP$_2$: $a = 6.1812$ Å, $b = 3.3455$ Å, $c = 8.2578$ Å and for ZrP$_2$: $a = 6.4940$ Å, $b = 3.5135$ Å and $c = 8.7434$ Å. An orthorhombic phase with the composition Ti$_{\sim 1.7}$P and the unit cell dimensions $a = 7.438$ Å, $b = 9.752$ Å and $c = 6.505$ Å is reported.

T HE Ti—P system has been the subject of an active interest in recent years, but knowledge of this system is nevertheless still far from complete. A further examination of this system has been made at this Institute and some new results have been obtained.

The present communication gives an account of some phase-analytical observations, and the crystal structure determinations of TiP$_2$ and ZrP$_2$ are described.

EXPERIMENTAL

Preparation. Phosphide samples were prepared from thin titanium turnings (claimed purity 99.8 %, less than 0.07 % oxygen) and red phosphorus (better than 99 %) by a special technique, previously described,[1] in order to reduce the possibilities for contamination of the reactants. The product was then arc melted in a purified argon atmosphere. This could be done with only a very small loss of phosphorus. Specimens produced in this way were used for the subsequent X-ray and microscopic investigation. The arc melted samples were heat treated in evacuated and sealed silica tubes at different temperatures between 450°C and 1000°C for times varying from a few days up to several weeks. Heat treatments at temperatures up to 1700°C were performed in an induction furnace with an atmosphere of purified argon.

Metallography. The system was studied metallographically, using a conventional grinding and polishing technique. The etching of the specimens presented considerable difficulties, as they were all very resistent to attack. In alloys containing up to 33 and more than 43 at. % phosphorus etching with dilute hydrofluoric acid proved satisfactory.

The results obtained for the alloys in the region 33—43 at. % phosphorus were not easy to interpret due to the difficulty of obtaining equilibrium.

Melting range determinations. The melting was carried out by induction heating in an atmosphere of purified argon. The specimens were suspended within a cylindrical tantalum susceptor by a tantalum wire which was supported axially in the furnace. An optical pyrometer was calibrated over the useful temperature range of the furnace by observing the melting of high purity copper, nickel, and platinum in an identical arrangement. The observed temperatures thus obtained included the correction necessary for the pyrometer and optical path whilst no emissivity correction was applied. The technique employed was to heat an alloy of given composition until visual signs of melting were observed. The accuracy is expected to be better than $\pm 50°C$.

X-Ray methods. The powder samples were investigated using a Guinier-Hägg type focussing camera with strictly monochromatic $CuK\alpha_1$ radiation $[\lambda(CuK\alpha_1) = 1.54051 \text{ Å}]$ and with silicon as internal standard ($a = 5.4305$ Å). An aluminium foil was used to reduce the fluorescence radiation from the samples. The intensities for TiP_2 and ZrP_2 were measured with a Philips powder diffractometer. Single-crystal investigations of Ti_2P and $Ti \sim_{1.7}P$ were made with a Weissenberg camera using zirconium-filtered MoK radiation. The Ti_2P diffraction pattern was also recorded in a Wiebenga integrating camera using $CuK\alpha$ radiation.

Electron-microprobe analysis. The use of solid metal pieces as a starting material resulted in the formation of a surface layer of reaction product which apparently acted as a diffusion barrier. Electron-microprobe traverses with a *Cambridge Geoscan* indicated that TiP was the only intermediate phase in the diffusion couple in specimens which had been treated with phosphorus from 1 day to 30 days.

Computing methods. All the calculations have been carried out on a *CDC* 3600 computer using the programs in Table 1.

THE Ti—P SYSTEM

Phase-studies

In a recent paper on the Ti—P system Lundström and Snell[1] summarized earlier investigations on the system. As no reliable phase diagram for the Ti—P system has been presented the present work was undertaken to provide

Table 1. All the calculations have been carried out on a CDC 3600 electronic computer using the following programs.

Program	Authors
Least squares refinement of unit-cell dimensions.	J. Tegenfeldt, Uppsala, Sweden.
Lorentz-polarization corrections.	R. Liminga, Uppsala, Sweden, modified by N.-O. Ersson, Uppsala, Sweden.
Fourier summations, structure factor calculations.	A. Zalkin, Berkeley, U.S.A., modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Least squares refinements of positional parameters and temperature factors.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A., modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Interatomic distances	A. Zalkin, Berkeley, U.S.A.

further information on the system and its intermediate phases. The principal features of the metal-rich part of the system were determined by the examination of as-cast alloy structures. A tentative phase diagram of the titanium-rich side could thereby be constructed. However, at the same time the system was also investigated by Yeremenko and Listovnichy.[2] Their results came only recently to the notice of the present author. Their findings are not fully supported in this investigation.

The formation of titanium phosphides is characterized by unusually slow reaction in the solid state. Direct combination of the elements using vapour diffusion techniques at temperatures at around 900°C proved to give the best result. This is in accordance with one of the so-called Hedvall-effects,[3] which states that the reactivity of a solid material is considerably increased in the region where a phase transformation takes place.

Attempts were made to determine the phase diagram by using diffusion experiments. Metal rods were heated with phosphorus at three temperatures 750°, 850°, and 950°C from 1 day to 30 days and the diffusion-zone was studied by the electron micro-probe technique. The only phase present in the zone was always TiP. The widest diffusion-zone, obtained after heat treatment at 950°C for 30 days, had the width 38 μm. If other phases were present their layers were too thin to be resolved unambiguously by the microprobe. The possibility of existing phases not showing up is the most obvious drawback of the interdiffusion method for determining phase diagrams. An examination of the diffusion-zone with an instrument with a higher resolution than the microprobe used (>2 μm) would perhaps reveal the other phases.

The Ti—P system has been investigated by Yeremenko and Listovnichy,[2] who used thermal analysis combined with microscopical and X-ray methods to study alloys containing up to 50 at. % phosphorus. In the alloys examined they found the phases Ti_3P, Ti_2P, Ti_3P_2, Ti_4P_3 and TiP. Their phase diagram for the region 0—33 and 43—50 at. % phosphorus is in agreement with the present investigation and is shown in Fig. 1. However, their results for the region 33—43 at. % phosphorus seem to be incomplete.

The present studies show the occurrence of a eutectic between β-titanium and Ti_3P at about 10 at. % phosphorus at a temperature of 1500°C. Ti_3P forms peritectically at 1770°C. Changes in the cell dimensions of Ti_3P were not observed within the limits of experimental errors. This applies to samples of different compositions and heat treatments up to 1000°C. Ti_2P forms peritectically at 1900°C. The Ti_2P lines have the same positions in all powder patterns for different compositions up to 1500°C, showing that the homogeneity range must be small. A metastable eutectic between Ti and Ti_2P was observed in arc melted alloys. Metastable eutectics in these types of alloys are very common. This phenomenon occurs for instance in the Fe—P system,[4] where an unstable Fe—Fe_2P eutectic has been observed, the peritectic formation of Fe_3P being entirely suppressed.

The phase diagram seems to be very complicated in the composition range Ti_2P—Ti_4P_3 and the powder patterns of the arc melted alloys were of great complexity. Since the arc melting produced alloys which were grossly inhomogeneous, annealing treatments at high temperatures were performed. In the region Ti_2P—Ti_5P_3 a new phase with a composition close to $Ti_{1.7}P$ was found.
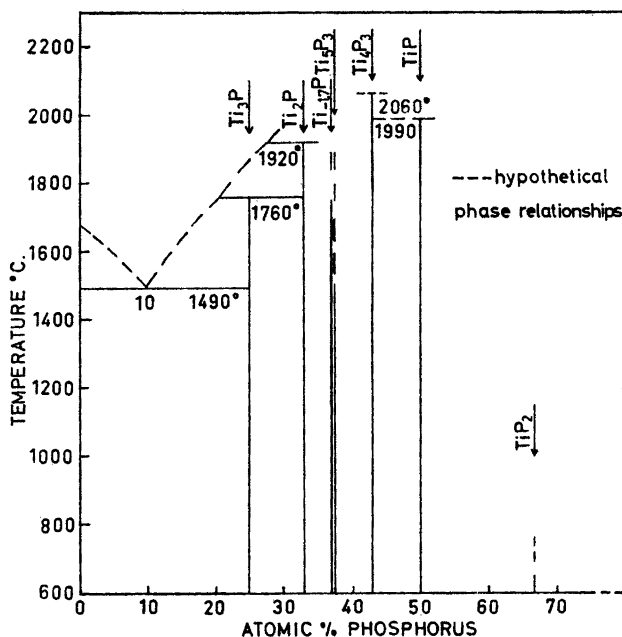
Fig. 1. Proposed phase diagram for the Ti—P system. For the region 0—33 and 43—50 at. % phosphorus the equilibrium diagram is as given by Yeremenko and Listovnichy.

This phase has been characterized crystallographically by a combination of single-crystal and powder methods (see below). In the composition range Ti_5P_3—Ti_4P_3 there is evidence for further subphosphides. Alloys in this region show many additional lines in the powder patterns when heat treated at temperatures above 1500°C, indicating that at least one new high temperature phase has been formed. Yeremenko and Listovnichy [2] were of the opinion that a phase which they denoted Ti_3P_2 (tetragonal with $a=7.483$ Å and $c=10.495$ Å) with a melting point maximum at 2098°C formed two-phase equilibria between Ti_2P and Ti_4P_3. These authors did not find Ti_5P_3 although this structure is stable up to at least 1500°C. Attempts to interpret the powder patterns for the region Ti_5P_3—Ti_4P_3 using the reported parameters for Ti_3P_2 have not yet been successful. According to the above cited authors Ti_4P_3 and TiP are formed peritectically, which is in accordance with the findings in the present investigation.

X - R a y i n v e s t i g a t i o n s

Ti₂P. Yeremenko and Listovnichy [2] reported that Ti_2P is isomorphous with Fe_2P. As a consequence of a structure proposed by Nowotny and Henglein,[5] they further described Ti_2P as trigonal with the cell dimensions $a=6.715$ Å and $c=3.462$ Å. The Fe_2P structure was subsequently revised by Rundqvist and Jellinek,[6] who showed that it has the hexagonal space group $P\bar{6}2m$.

In a recent paper Lundström and Snell[1] reported a new hexagonal phase with a composition not far from Ti_2P. A least-squares refinement of the powder diffraction data resulted in the following unit cell dimensions and standard deviations:

Ti-rich, 900°C $a = 11.5314 \pm 0.0015$ Å
$c = 3.4575 \pm 0.0009$ Å
P-rich, 900°C $a = 11.5276 \pm 0.0018$ Å
$c = 3.4580 \pm 0.0012$ Å

It proved difficult to obtain single crystals of Ti_2P suitable for single crystal investigations. The crystals obtained from the melt were needle-shaped aggregates of extremely small size. Finally, a very small single crystal with the dimensions $0.012 \times 0.005 \times 0.005$ mm was selected for the X-ray investigation. It was mounted in a Weissenberg camera with the c axis as the rotation axis. The Laue symmetry of the crystal proved to be $P6/mmm$, and no systematical absences were observed for the hkl reflexions. A possible systematic extinction was indicated by the powder photographs from which the 001 and 003 reflexions were absent while 002 appeared strong. The fact that the c axis is very short, and the ratio $F_o(hk0)/F_o(hk2)$ is constant within the experimental errors, indicates that the atoms are confined to two planes perpendicular to the c axis and spaced $c/2$ apart.

A crystal structure investigation of Ti_2P is currently being undertaken at this institute.

$Ti \sim 1.7P$. A preliminary X-ray investigation of the $Ti \sim 1.7P$ crystals showed that the symmetry is orthorhombic. The crystals obtained from the melt were plate-shaped and severely intergrown. For the X-ray investigation a single crystal fragment was used. Approximate unit cell dimensions were determined from oscillation and Weissenberg photographs. Using the symmetry information and the approximate unit cell dimensions obtained from the single crystal films the lines in powder diffraction films recorded in a Guinier-Hägg type focussing camera were indexed. All powder patterns of samples containing $Ti \sim 1.7P$ showed line-broadening effects. The following values for the cell parameters and their standard deviations were obtained after a least-squares refinement:

$a = 7.4376 \pm 0.0014$ Å
P-rich, 900°C $b = 9.7522 \pm 0.0014$ Å
$c = 6.5047 \pm 0.0011$ Å

No systematical extinctions of hkl reflexions could be detected. This indicates a primitive cell. The $h00$, $0k0$ and $00l$ reflexions were present only when $h=2n$, $k=2n$, and $l=2n$, respectively. These conditions are satisfied for the unique space group $P2_12_12_1$.

Ti_4P_3. Yeremenko and Listovnichy[2] found this phase to be cubic with $a=7.425$ Å, which is in accordance with the findings in the present investigation. A least-squares refinement of a powder pattern, whith the nominal composition $Ti_{1.3}P$ and heat treated at 900°C for 7 days resulted in the following parameter:

$a = 7.4298 \pm 0.0003$ Å

Table 2a. Powder data for Ti$_{\sim 1.7}$P. (CuKα_1 radiation).

hkl	sin$^2\theta_{obs} \times 10^5$	sin$^2\theta_{calc} \times 10^5$	I_0
021	3 892	3 897	w—
031	7 029	7 017	w— —
112	7 308	7 305	w— —
221	8 194	8 188	m
202	9 903	9 899	w—
040	9 981	9 981	w
301	11 052	11 055	m
032	11 227	11 223	st
231	11 302	11 307	st
041	11 381	11 383	st
311	11 682	11 679	w—
222	12 390	12 394	st
013	13 240	13 244	m
240	14 268	14 271	m

Table 2b. Powder data for Ti$_4$P$_3$. (CuKα_1 radiation).

hkl	sin$^2\theta_{obs} \times 10^5$	sin$^2\theta_{calc} \times 10^5$	I_0
220	8 592	8 598	w
310	10 748	10 748	st+
321	15 053	15 047	st
420	21 483	21 495	w
332	23 636	23 645	w—
422	25 792	25 793	m—
431 510	27 939	27 944	m
532 611	40 856	40 842	m·
620	42 988	42 991	w
541	45 145	45 141	w+

The line intensities of the Ti$_4$P$_3$ powder pattern indicate strongly that Ti$_4$P$_3$ is antistructural with Th$_3$P$_4$.

For identification purposes, powder diffraction data for Ti$_{\sim 1.7}$P and Ti$_4$P$_3$ are given in Table 2.

THE CRYSTAL STRUCTURE OF TiP$_2$

Attempts to prepare single-crystals of TiP$_2$ suitable for X-ray examination were unsuccessful. Heat treatments for very long periods of time between 450°C and 900°C, and experiments with halogen transport technique were tried. Neither transport nor mineralisation of TiP$_2$ took place in these experiments. The crystallographic examination of TiP$_2$ therefore had to be performed by powder diffraction methods.

Intensities of the reflexions were measured with a Philips powder diffractometer using CuK radiation. A LiF-crystal monochromator was used in the diffracted beam. This arrangement had the advantage of eliminating undesirable fluorescence radiation and improving the signal-to-noise ratio.

The polarization correction for X-rays rendered monochromatic by a crystal has been treated by Azároff.[7] A small modification of his treatment results in an expression for the Lorentz-polarisation factor that becomes

$$\frac{(1 + \cos^2 2\theta_1 \cdot \cos^2 2\theta_2)}{(1 + \cos^2 2\theta_1)(8\sin^2\theta_2 \cdot \cos\theta_2)}$$

where $2\theta_1$ is the diffraction angle in the specimen and $2\theta_2$ is the diffraction angle in the monochromator. This expression was used for the Lp-correction.

In order to minimize the effects of preferred orientation the powder was mounted according to a method proposed by McCreery.[8] Rotation of the specimen in its own plane had no significant effect on the average intensity, which indicated that the second-order preferred orientation within the specimen plane was avoided. The overlaps among the reflexions were rather numerous and only 19 well resolved reflexions could be measured with acceptable accuracy.

In the calculation of structure factors, atomic scattering factors were obtained from Ref. 9 while the real part of the anomalous dispersion correction used was taken from Ref. 10. After some preliminary calculations a full-matrix least-squares refinement of the positional parameters, three isotropic temperature factors and one scale factor was finally made. Following a suggestion by Cruickshank et al.[11] a weighting scheme according to the formula $w=1/(a+|F_o|+c|F_o|^2)$ was employed with the constants $a=30.0$ and $c=0.02$. The refinement converged rapidly and the final R-value was 0.054. The largest shifts in the parameters were less than 0.004 % of the standard deviations.

The final structure data for TiP_2 is given in Table 3. Interatomic distances shorter than 4.0 Å are listed in Table 4. The temperature factors for the atoms in TiP_2 (see Table 3) do not have any physical meaning. A refinement with all the temperature factors fixed to $B=0.25$ Å² did not produce significant changes in the positional parameters, whereas the R-value was somewhat increased.

It is difficult to assess the accuracy of this structure determination. Although the parameters in Tables 3 and 4 (temperature factors excluded) have reasonable values they should be regarded with caution since only a small number of reflexions were used in the refinement.

Table 3. Final structure data for TiP_2.

Space-group $Pnma - (D_{2h}^{16})$, (No. 62)
All atoms in 4(c) positions.

$$a = 6.1812 \text{ Å} \qquad \sigma(a) = 0.0006 \text{ Å}$$
$$b = 3.3455 \text{ Å} \qquad \sigma(b) = 0.0004 \text{ Å}$$
$$c = 8.2578 \text{ Å} \qquad \sigma(c) = 0.0009 \text{ Å}$$

Atom	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Ti	0.2747	0.0065	0.1559	0.0024	2.36	0.58
P_I	0.8916	0.0022	0.0428	0.0029	−2.64	0.95
P_{II}	0.9236	0.0061	0.6266	0.0030	−0.29	0.97

Table 4. Interatomic distances and their standard deviations (Å units) in TiP_2. Distances shorter than 4 Å listed.

	Dist.	S.d.		Dist.	S.d.
Ti—1 P_{II}	2.508	0.036	P_{II}—1 Ti	2.508	0.036
—2 P_{II}	2.517	0.041	—2 Ti	2.517	0.041
—1 P_I	2.546	0.041	—2 P_I	2.659	0.031
—2 P_I	2.559	0.026	—2 Ti	2.744	0.032
—1 P_I	2.591	0.032	—2 P_{II}	2.839	0.044
—2 P_{II}	2.744	0.032	—1 P_I	3.213	0.039
—2 Ti	3.346	0.000	—2 P_{II}	3.346	0.000
—2 Ti	3.459	0.018	—2 P_I	3.400	0.031
—1 P_I	3.926	0.042	—1 P_I	3.443	0.034
			—1 P_I	3.574	0.039
P_I—2 P_I	2.257	0.022	—2 P_{II}	3.702	0.027
—1 Ti	2.546	0.041			
—2 Ti	2.559	0.026			
—1 Ti	2.591	0.032			
—2 P_{II}	2.659	0.031			
—1 P_{II}	3.213	0.039			
—2 P_I	3.346	0.000			
—2 P_{II}	3.400	0.031			
—1 P_{II}	3.443	0.034			
—1 P_{II}	3.574	0.039			
—1 Ti	3.926	0.042			

THE CRYSTAL STRUCTURE OF ZrP_2

Since it was impossible to obtain single-crystals of ZrP_2, the crystallographic examination was performed by powder diffraction methods.

Intensities for the reflexions were measured with a Philips powder diffractometer using $CrK\alpha$ radiation. The specimen was rotated rapidly (85 rpm) in its own plane in order to increase the precision in the intensity measurement. 51 reflexions could be measured with acceptable accuracy. The high-angle reflexions for ZrP_2 were not as severly overlapped as for TiP_2. This made it possible to use a much greater number of reflexions in the refinement of ZrP_2.

On the basis of the atomic parameters obtained from $MoGe_2$,[12] the refinement by least-squares was started directly. The constants in Cruickshank's

Table 5. Final structure data for ZrP_2.

Space-group *Pnma* — (D_{2h}^{16}), (No. 62)
All atoms in 4(c) positions.

$$a = 6.4940 \text{ Å} \qquad \sigma(a) = 0.0005 \text{ Å}$$
$$b = 3.5130 \text{ Å} \qquad \sigma(b) = 0.0003 \text{ Å}$$
$$c = 8.7440 \text{ Å} \qquad \sigma(c) = 0.0005 \text{ Å}$$

Atom	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Zr	0.2820	0.0010	0.1590	0.0007	0.12	0.32
P_I	0.8853	0.0026	0.0405	0.0021	—0.28	0.66
P_{II}	0.9121	0.0037	0.6402	0.0027	1.01	0.59

Table 6. Interatomic distances and their standard deviations (Å units) in ZrP_2. Distances shorter than 4 Å listed.

	Dist.	S.d.		Dist.	S.d.
$Zr-2\ P_{II}$	2.657	0.019	$P_{II}-2\ Zr$	2.657	0.019
$-2\ P_I$	2.704	0.015	$-1\ Zr$	2.749	0.024
$-1\ P_I$	2.711	0.019	$-2\ P_I$	2.752	0.023
$-1\ P_{II}$	2.749	0.024	$-2\ Zr$	2.785	0.019
$-1\ P_I$	2.777	0.018	$-2\ P_{II}$	3.225	0.040
$-2\ P_{II}$	2.785	0.019	$-1\ P_1$	3.456	0.029
$-2\ Zr$	3.513	0.000	$-1\ P_I$	3.505	0.030
$-2\ Zr$	3.616	0.006	$-2\ P_{II}$	3.513	0.000
			$-2\ P_I$	3.551	0.026
$P_I-2\ P_I$	2.410	0.024	$-1\ P_I$	3.768	0.029
$-2\ Zr$	2.704	0.015	$-2\ P_{II}$	3.773	0.024
$-1\ Zr$	2.711	0.019			
$-2\ P_{II}$	2.752	0.023			
$-1\ Zr$	2.777	0.018			
$-1\ P_{II}$	3.456	0.029			
$-1\ P_{II}$	3.505	0.030			
$-2\ P_I$	3.513	0.000			
$-2\ P_{II}$	3.551	0.026			
$-1\ P_{II}$	3.768	0.029			

formula were finally given the values $a=40.0$ and $c=0.006$. The refinement converged rapidly and the final R-value was 0.072. The atomic parameters, individual temperature factors, and their standard deviations are listed in Table 5. Interatomic distances shorter than 4.0 Å are listed in Table 6.

DESCRIPTION AND DISCUSSION OF THE TiP_2 AND ZrP_2 STRUCTURES

A projection of the TiP_2 structure on the ac plane is shown in Fig. 2. The titanium atoms are surrounded by six phosphorus atoms at the corners of a
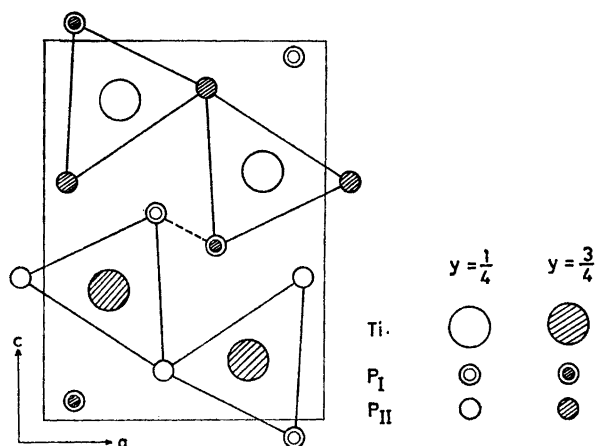

Fig. 2. The crystal structure of TiP_2 projected on (101).

triangular prism, and three phosphorus atoms outside each rectangular side of the prism forming a triangle around the titanium atoms. The average of the four Ti—Ti distances is 3.40 Å, exceeding the Goldschmidt metal diameter for 12-coordination (2.90 Å) by 17 %. The phosphorus atom P_I is surrounded by two near phosphorus neighbours (P_I) and four near titanium neighbours arranged in a slightly deformed tetrahedral configuration. The mean value of the four P_I—Ti distances is 2.56 Å, which corresponds well to the sum of the Goldschmidt radius for titanium and the tetrahedral covalent radius for phosphorus (1.10 Å). The P_{II} atom is surrounded by five near titanium atoms in a distorted square pyramidal arrangement, the average P_{II}—Ti distances being 2.61 Å. The phosphorus atoms in TiP_2 are linked together (P—P distances 2.26 Å) forming infinite zig-zag chains (indicated with pecked lines in Fig. 2) extending in the b direction, the other P—P distances being 2.61 Å or longer.

In ZrP_2 the average of the four Zr—Zr distances is 3.56 Å, which exceeds the Goldschmidt metal diameter (3.20 Å) by 11 %. The mean value for the four P_I—Zr distances is 2.72 Å and for the five P_{II}—Zr distances likewise 2.72 Å, which corresponds well to the radius sum. The short P—P distances in the chains along the b axis are 2.41 Å, the other P—P distances being 2.75 Å or longer.

The structures of the transition metal diphosphides are all characterized by short P—P contacts. The only exception known at present is UP_2 in which there are no P—P distances shorter than 2.7 Å. The short distances in TiP_2 (2.26 Å) and ZrP_2 (2.41 Å) both exceed the normal bonding distance of 2.2 Å. In the isostructural $ZrAs_2$[13] chains are also formed the As—As distances being 2.59 Å, which again exceeds the normal bonding distance of 2.42 Å.

From simple geometrical considerations the formation of short P—P contacts should become more favourable the larger the r_P/r_{Me} radius ratio. In ZrP_2 the tendency to form short P—P distances is thus counteracted by the unfavourable radius ratio, which leads to the formation of longer P—P distances.

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