Studies of Crystal Structures and Phase Relationships in the Ti-P System

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The crystal structures of Ti_3P and Ti_5P_3 have been refined using single crystal X-ray methods. A discussion of the Ti_3P structure is included.

A new hexagonal phase with a composition not far from Ti_2P has been prepared and has the unit cell dimensions $a = 11.530$ Å and $c = 3.458$ Å. It has been synthesized by a special technique in order to reduce the possibilities for contamination of the reactants.

Accurate cell dimensions for Ti_3P, Ti_5P_3, TiP, and TiP_2 are also reported.

Some years ago Ti_3P was stated to belong to the Fe_3P type structure by Schönberg.[1] However, one of the present authors[2] found that Ti_3P is of the ε_1 (Fe-P-B)-type structure, which was determined by Rundqvist.[3] As Ti_3P was the first binary ε_1-compound discovered it was thought desirable to determine the interatomic distances accurately. The designation Ti_3P type structure instead of ε_1 type has been recommended by Dr. Rundqvist and will be adopted from now on. It has also already been used by Schubert.[4]

In conjunction with the single crystal investigation of Ti_3P, phase analytical studies of the Ti-P system were also made. As early as 1963 we collected single-crystal intensity data from a new phase, which later proved to be Ti_5P_3. However, this phase was also discovered at the same time by Brauer and collaborators in Freiburg.[5] Later they have published papers on the synthetical aspects of the Ti-P system[6] as well as a very accurate crystal structure determination of Ti_5P_3.[7] This paper reports the results of the refinements of Ti_3P and Ti_5P_3. Furthermore some new data for the Ti-P system are given.

EXPERIMENTAL

Preparation. Ti_3P was prepared from thin titanium turnings and red phosphorus. The reactants were sealed under vacuum in a silica capsule and simultaneously heated and shaken in a furnace, constructed by Dr. Allan Brown of this Institute. After heating at 850°C for 48 h no unreacted phosphorus was visible. Microscopic and X-ray investigations showed, however, that the product was inhomogeneous, the titanium turnings
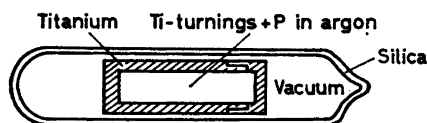
Titanium   Ti-turnings + P in argon

Silica

Vacuum

Fig. 1. Arrangement for the reaction between titanium turnings and red phosphorus.

having a core of titanium, surrounded by a layer of TiP. 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, contained single crystals which were subsequently used for the refinement of the Ti_3P and Ti_5P_3 structures.

There is, however, a danger of reaction between the reactive titanium metal and the silica capsule in this process. To eliminate this an alternative method was used, where the reaction was performed inside a closed titanium cylinder with a tightly screwed lid (Fig. 1). The reactants were packed into the titanium cylinder under a slight over-pressure of argon. The cylinder was then closed and rapidly put into the silica tube, which was then sealed under vacuum. In this way a close control of the composition of the sample is made more difficult but the risk of introducing impurities during preparation is undoubtedly kept down to a minimum. Alloys prepared in this way gave single crystals of Ti_3P and have also been used for the phase analysis described below. During the heat treatments the samples were always protected from direct contact with the silica capsule through an inner crucible of titanium or alumina.

Chemical analysis. No chemical analysis of the final products was made. The original titanium had the following analysis 99.8 % Ti, 0.1 % Fe, 0.066 % O, 0.006 % N, 0.002 % H. The red phosphorus used contained more than 99 % P.

X-Ray methods. The powder samples were investigated using a Guinier-Hägg type focussing camera with strictly monochromatic $CuK\alpha_1$ radiation [$\lambda(CuK\alpha_1) = 1.54051$ 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 cell dimensions of the Ti_5P_3 crystal were determined with a General Electric Single Crystal Orienter, the zero point on the 2θ scale being known from a calibration with a crystal of basic beryllium acetate.

Intensity data for the single crystal investigations were recorded with an equi-inclination Weissenberg camera using Nb-filtered $MoK\alpha$ radiation. The multiple film technique with thin iron foils between successive films was used. The intensities were estimated visually by comparison with a calibrated scale.

For the refinement of the crystal structure of Ti_3P a plate-shaped single crystal with the dimensions $0.170 \times 0.108 \times 0.023$ mm was picked from the arc-melted alloy. Only two layer lines, $hk0$ and $h0l$, were recorded. An absorption correction was applied, assuming a somewhat idealized shape of the crystal and $\mu = 94$ cm^{-1}. The improvement resulting from this correction was, however, very moderate. For Ti_5P_3 no absorption correction was applied, as the crystal was smaller than that of Ti_3P. Furthermore only $hk0$ reflexions were used.

Computing methods. Correction for absorption, Fourier summations, calculations of structure factors and interatomic distances were made on the Swedish computer Facit using programs 6019, 6014, 6015, and 6016 in the *IUCr World List of Crystallographic Computer Programs.*[8] The least squares refinements were made with program 360 in the list.[8] The correction for Lorentz and polarization factors was made on Facit with a program by Lundberg.[9] The atomic scattering factors used were taken from Table 3.3.1A of the *International Tables.*[10] The real part of the dispersion correction, given in table 3.3.2C,[10] was also included. The least squares refinement of the lattice parameters was made with a program called CELSIUS, written by J. Tegenfeldt[11] for a CDC 3600 computer. This program minimizes the function

$$R = \sum_i w_i \left\{ \frac{\sin^2\theta_{i,\text{obs}}}{\lambda_i^2} - \frac{\sin^2\theta_{i,\text{calc}}}{\lambda_i^2} \right\}$$

with

$$w_i = u\theta_i \cdot \frac{\lambda_i^4}{\sin^2 2\theta_i}$$

The weight w_i is dependent only on the absolute error in measuring θ_i, e.g. the precision in locating the reflexion on the film and the precision by which this measurement can be related to a θ-value.

THE Ti-P SYSTEM

Earlier investigations of the Ti-P system were summarized by Hansen [12] and by Elliott.[13] The existence of TiP and a subphosphide was reported by Biltz, Rink and Wiechmann as the result of a mainly tensimetric investigation.[14] The structure of TiP was determined by Schönberg,[15] who also reported that the existence of TiP_2 was confirmed, although no earlier report of this compound is known. The first X-ray characterization of TiP_2 was made by Hulliger.[16]

In a paper on the ternary system Fe-Ti-P Vogel and Giessen [17] gave an outline of the binary phase diagram of the Ti-P system indicating only one intermediate phase, namely TiP. As will be shown below there is now convincing evidence for the existence of four or five further phases in the system. Thus no reliable phase diagram for the Ti-P system has been presented. As a guide to the following presentation of our phase analytical work the X-ray data for all phases prepared by us are collected in Table 1.

Table 1. Unit cell dimensions and standard deviations for phases in the Ti-P system, as determined in the present investigation.

Phase	Preparation	Structure type	No. of refl.	Cell dimensions (Å)		Cell volume (Å³)
Ti_3P	Arc-melted	Ti_3P	43	$a =$	9.9592 ± 0.0005	494.6 ± 0.1
				$c =$	4.9869 ± 0.0004	
Ti_2P	Ti-rich, 900°C	Hexagonal	16	$a =$	11.5314 ± 0.0015	398.2 ± 0.2
				$c =$	3.4575 ± 0.0009	
	P-rich, 900°C		14	$a =$	11.5276 ± 0.0018	398.0 ± 0.3
				$c =$	3.4580 ± 0.0012	
Ti_5P_3	Arc-melted, powder	Mn_5Si_3	23	$a =$	7.2297 ± 0.0006	230.6 ± 0.1
				$c =$	5.0950 ± 0.0007	
	Arc-melted, single crystal		11	$a =$	7.2226 ± 0.0007	230.1 ± 0.1
				$c =$	5.0936 ± 0.0008	
TiP	Ti-rich, 900°C	TiP	8	$a =$	3.4991 ± 0.0006	124.1 ± 0.1
				$c =$	11.7025 ± 0.0016	
	P-rich, 700°C		12	$a =$	3.4988 ± 0.0012	124.0 ± 0.2
				$c =$	11.7000 ± 0.0055	
TiP_2	650°C	$PbCl_2$	12	$a =$	6.1812 ± 0.0006	170.8 ± 0.1
				$b =$	8.2578 ± 0.0009	
				$c =$	3.3455 ± 0.0004	

Changes in the cell dimensions of Ti_3P were not observed within the limits of experimental errors. This holds for samples of different compositions and heat treatments up to 1000°C. Neither was any sign of polymorphic transition (for instance to the Fe_3P-type structure) in Ti_3P observed.

A hexagonal phase with a composition not far from Ti_2P was found in samples prepared in a closed titanium cylinder. At 900°C no variations in cell dimensions were observed. A single crystal of this phase is now under investigation at this Institute. In earlier investigations by Vereikina and Samsonov [18] and by Biltz et al.[14] indications for a Ti_2P phase were found. However, lack of details in their characterization of the phase makes it impossible to establish whether this is the same phase or not.

Variations in the cell dimensions of Ti_5P_3 greater than those given in Table 1 are observed, although the reproducibility is not satisfactory. This fact together with the well-known tendency of the Mn_5Si_3-type structure to accomodate non-metal atom impurities in the lattice [19,20] is taken as an indication that Ti_5P_3 may easily become contaminated during preparation. This interpretation does not, of course, preclude a variation of the phosphorus content.

Films from samples in the region $Ti_2P-Ti_{1.6}P$ invariably show extra lines. Thus there is evidence for the occurrence of a further subphosphide probably between Ti_2P and Ti_5P_3. Attempts to index the lines have not yet been successful.

As shown in Table 1 the cell dimensions of TiP do not differ significantly as measured in two-phase samples on both sides of TiP, heat treated between 700—900°C. Accordingly, at this temperature the investigation does not support earlier reports [6,14] of a considerable homogeneity range for TiP. The lattice parameters of TiP_2 are in excellent agreement with those given by Hulliger.[16]

The formation of titanium phosphides is characterized by unusually slow reactions in the solid state. TiP is invariably formed as the first phosphide whatever the starting composition of the reaction mixture. This was also observed by Knausenberger et al.[6] A favourable kinetic factor might be the explanation of this, as the thermal stability of the subphosphides is very high; the melting (or decomposition) temperature of Ti_2P being higher than 1700°C. In view of this, the observation of Biltz et al.[14] that the X-ray diagram of the subphosphide had a number of lines in common with that of TiP, seems to be best explained by the assumption that all samples between Ti and TiP contained some TiP.

Finally a peculiarity in the densities of the three phases Ti_3P, Ti_2P, and Ti_5P_3 might be mentioned. The calculated densities are 4.69, 4.76, and 4.84 g/cm³, respectively, for the three phases assuming a cell content of 18 Ti and 9 P for Ti_2P. All three values are higher than the value of 4.52 g/cm³ for hexagonal close-packed titanium metal.

THE STRUCTURE OF Ti_5P_3

Starting with the reported parameters,[7] a least squares refinement was performed with the weighting scheme [21]

$$w = 1/(a + |F_o| + c|F_o|^2)$$

with $a = 22.0$ and $c = 0.025$. (The four strongest reflexions *410, 300, 210, 440* were excluded as suffering from extinction). A list of observed and calculated structure factors for Ti_5P_3 as well as for Ti_3P can be obtained from this Institute on request. With the occupational parameter of position 2(*b*) given in Table 2 a final difference synthesis was calculated. The result was a relatively even map.

Table 2 presents the results together with those of Bärnighausen *et al.*[7] and a least squares refinement of their data (the same weighting scheme being used with $a = 11.0$ and $c = 0.015$). The degree of occupation in position 2(*b*) was also varied in the least squares refinements.

In general there are no great differences between the two determinations. The only important deviation is found in the octahedral positions along the hexagonal axis. In our case the octahedral position possibly shows a higher electron density, although the cell volume is less. The octahedron is also slightly deformed with Ti—Ti distances along the hexagonal axis 3.100 Å and Ti—Ti distances perpendicular to it 3.063 Å as compared to the values 3.110 Å and 3.114, respectively, in the determination of Bärnighausen *et al.*[7] The distance from the center of the octahedron to its corners, 2.18 Å, is very much smaller than the radius sum for titanium (1.45 Å) and phosphorus (1.10 Å) but not far from that of titanium and oxygen (0.66 Å) or nitrogen (0.70 Å).

Table 2. Structure data for Ti_5P_3. Space group $P6_3/mcm$.

	As given by Bärnig-hausen *et al.*[7]	L. sq. refinement of the data in Ref. 7 with standard deviations	L. sq. refine-ment of own data with standard dev.
a (Å)	7.2381 ± 0.0005		7.2226 ± 0.0007
c (Å)	5.088 ± 0.003		5.0936 ± 0.0008
V (Å³)	230.9 ± 0.2		230.1 ± 0.1
4Ti(1) in 4(*d*)			
$B_x = B_y$	0.18	0.22 ± 0.01	} 0.26 ± 0.04
B_z	0.36	0.42 ± 0.05	
6Ti(2) in 6(*g*)			
x	0.24806 ± 0.00009	0.24786 ± 0.0001	0.2448 ± 0.0006
B_x	0.35	0.35 ± 0.013	}
B_y	0.19	0.22 ± 0.013	} 0.29 ± 0.05
B_z	0.43	0.51 ± 0.04	}
6P(1) in 6(*g*)			
x	0.60773 ± 0.00014	0.60783 ± 0.00015	0.6052 ± 0.0008
B	0.31	0.28 ± 0.02	}
B_y	0.20	0.20 ± 0.02	} 0.21 ± 0.08
B_z	0.63	0.63 ± 0.04	}
aP(2) in 2(*b*)			
$B_x = B_y$	0.25	0.34 ± 0.014	} 1.3 ± 0.8
B_z	0.6	2.1 ± 0.7	}
a	0.15 (±0.025)	0.17 ± (0.03)	0.31 ± 0.06
No. of refl.	324	324	52
R-value (%)	4.1	4.1	7.3

Table 3. Interatomic distances in Ti_5P_3 with standard deviations (both in Å).

Atoms	According to Bärnighausen et al.[7] Estimated accuracy ± 0.004 Å	This investigation
Ti(1) — 2Ti(1)	2.544	2.547 ± 0.000
6Ti(2)	3.051	3.060 ± 0.003
6P (1)	2.567	2.558 ± 0.002
Ti(2) — 4Ti(1)	3.051	3.060 ± 0.003
2Ti(2)	3.110	3.063 ± 0.008
4Ti(2)	3.114	3.100 ± 0.002
2P (1)	2.487	2.493 ± 0.005
1P (1)	2.603	2.603 ± 0.007
2P (1)	2.750	2.768 ± 0.003
P (1) — 2Ti(2)	2.487	2.493 ± 0.005
4Ti(1)	2.567	2.558 ± 0.002
1Ti(2)	2.603	2.603 ± 0.007
2Ti(2)	2.750	2.768 ± 0.003
2P (1)	2.984	2.966 ± 0.006
2P (2)	3.110	3.123 ± 0.005
P (2) — 6Ti(1)	2.200	2.179 ± 0.004
2P (2)	2.544	2.547 ± 0.000
6P (1)	3.110	3.123 ± 0.005

Thus it seems probable that part of the electron density in the octahedral hole, at least in our crystal, might be ascribed to oxygen or nitrogen (see Table 3).

The phosphorus atom P(2) is characterized by a large value of B_z but normal values of B_x and B_y. This is in agreement with the fact that only B_z can reflect the disorder in the partly filled 2(b) position. For a more detailed discussion of the structure and further references see Bärnighausen et al.[7]

THE DETERMINATION OF THE Ti_3P STRUCTURE

Initially a Fourier projection was computed using only 50 of the strongest observed $h0l$ reflexions and the signs from an F_c-calculation made with the atomic coordinates given by Rundqvist for ε_1(Fe-P-B).[3] The coordinates returned from this Fourier projection were then used as starting coordinates in the least squares refinement with isotropic temperature factors and Cruickshank's weighting function with $a = 5.3$ and $c = 0.009$. 269 reflexions were used in the refinement, only the strong *004* reflexion being omitted as suffering from extinction. After 4 cycles the shifts were very small and the R-value (defined as $R = \sum ||F_o| - s_q|F_c||/|F_o|$) was then 0.063. The $h0l$ difference projection was finally computed, in which the largest maxima (or minima) were less than 4 % of the titanium maxima in the electron density map.

The atomic coordinates together with their calculated standard deviations are given in Table 4 and the interatomic distances less than 4 Å are found in Table 5.

Table 4. Atomic coordinates for Ti_3P based on space group $P4_2/n - (C_{4h}{}^4)$. No. 86. Origin at $\bar{1}$.

Atom	X $\pm$ $\sigma(X)$	Y $\pm$ $\sigma(Y)$	Z $\pm$ $\sigma(Y)$	B $\pm$ $\sigma(B)$ Å²
Ti(1)	0.16613 $\pm$ 0.00025	0.64275 $\pm$ 0.00026	0.7153 $\pm$ 0.0012	0.292 $\pm$ 0.028
Ti(2)	0.11009 $\pm$ 0.00027	0.27849 $\pm$ 0.00023	0.5295 $\pm$ 0.0011	0.247 $\pm$ 0.027
Ti(3)	0.06957 $\pm$ 0.00024	0.53342 $\pm$ 0.00025	0.2407 $\pm$ 0.0011	0.224 $\pm$ 0.027
P	0.04395 $\pm$ 0.00042	0.29188 $\pm$ 0.00043	0.0354 $\pm$ 0.0021	0.252 $\pm$ 0.045

DISCUSSION OF THE Ti_3P STRUCTURE

A detailed description and discussion of the Fe_3P and ε_1 structures was given elsewhere by Rundqvist.[3,22] The present discussion is confined to a comparison of the three isostructural compounds Ti_3P, Zr_3P, and Nb_3P. The refinements of the last two structures were recently published by Nawapong.[23]

A very convenient way of describing the Ti_3P structure is as a packing of more or less regular PTi_9 tetrakaidecahedra. Each such unit consists of a central atom (C), surrounded by six atoms (A) at the corners of a triangular prism, the basal triangles of which are $A_1—A_3—A_5$ and $A_2—A_4—A_6$, and three atoms (B) outside the rectangular faces of the prism (Fig. 2). The C atom is the phosphorus atom while the A and B atoms are metal atoms. A classification of the observed interatomic distances according to these nota-

Table 5. Interatomic distances in Ti_3P with standard deviations. Distances less than 4 Å are listed.

| Atoms		Distance (Å)	Atoms	Distance (Å)
Ti(1)—	Ti(1)	2.712 $\pm$ 0.005	Ti(2)—Ti(3)	3.702 $\pm$ 0.004
	Ti(3)	2.777 $\pm$ 0.007		
	Ti(3)	2.939 $\pm$ 0.004	Ti(3)—Ti(3)	2.850 $\pm$ 0.010
	Ti(3)	2.996 $\pm$ 0.007	Ti(3)	3.009 $\pm$ 0.010
	Ti(2)	3.035 $\pm$ 0.005		
	Ti(3)	3.082 $\pm$ 0.004	P —Ti(3)	2.490 $\pm$ 0.008
	Ti(2)	3.110 $\pm$ 0.005	Ti(1)	2.519 $\pm$ 0.007
4	Ti(1)	3.146 $\pm$ 0.002	Ti(2)	2.551 $\pm$ 0.005
	Ti(3)	3.158 $\pm$ 0.004	Ti(2)	2.552 $\pm$ 0.005
	Ti(2)	3.786 $\pm$ 0.004	Ti(2)	2.554 $\pm$ 0.012
			Ti(1)	2.567 $\pm$ 0.007
Ti(2)—	Ti(3)	2.833 $\pm$ 0.005	Ti(3)	2.597 $\pm$ 0.007
	Ti(2)	2.844 $\pm$ 0.005	Ti(2)	2.611 $\pm$ 0.012
	Ti(3)	2.861 $\pm$ 0.005	Ti(3)	2.627 $\pm$ 0.006
	Ti(3)	2.947 $\pm$ 0.005	Ti(3)	3.890 $\pm$ 0.006
2	Ti(2)	2.980 $\pm$ 0.009	2P	3.654 $\pm$ 0.013
2	Ti(2)	3.437 $\pm$ 0.009		
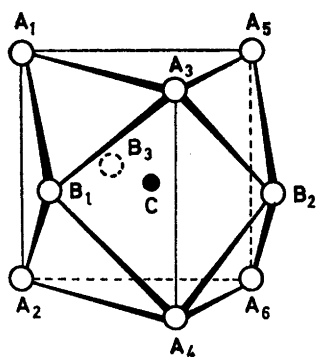
Fig. 2. A non-metal atom C, tetrakaideca-
hedrally surrounded by nine metal atoms.

Table 6. Interatomic distances (Å) in Ti_3P, Nb_3P, and Zr_3P arranged according to the tetrakaidecahedral description. Data for Nb_3P and Zr_3P from Ref. 23.

Distance type	Ti_3P	Nb_3P	Zr_3P
$A_1A_3 = A_3A_5$	3.437	3.405	3.660
A_1A_5	2.844	2.946	3.022
A_2A_4	3.146	3.154	3.401
A_2A_6	3.082	3.182	3.338
$A_4A_6 = B_1A_2$	2.996	3.061	3.201
A_1A_2	3.786	4.132	4.100
A_3A_4	3.110	3.100	3.377
A_5A_6	3.702	3.527	4.140
$B_1A_1 = B_2A_3$	2.947	3.140	3.214
$B_1A_2 = A_4A_6$	2.777	2.931	2.982
$B_1A_3 = B_2A_5$	2.861	2.833	3.088
B_1A_4	3.158	3.189	3.407
B_2A_4	2.939	2.966	3.193
B_2B_6	2.850	2.819	3.052
$B_3A_1 = B_3A_5$	2.980	3.175	3.201
B_3A_2	3.035	3.100	3.317
B_3A_6	2.833	2.903	3.103
A_1C	2.551	2.618	2.739
A_2C	2.567	2.592	2.765
A_3C	2.554	2.607	2.754
A_4C	2.519	2.569	2.734
A_5C	2.552	2.549	2.745
A_6C	2.490	2.534	2.678
B_1C	2.597	2.635	2.813
B_2C	2.627	2.888	2.863
B_3C	2.611	2.643	2.809

tions is given in Table 6 for Ti_3P as well as for Zr_3P and Nb_3P. It should be noted that further short metal-metal distances exist between adjacent tetra-kaidecahedra.

Table 7. Average interatomic distances d_{AA}, d_{AB}, d_{AC}, and d_{BC} in some Me_3P phases. Radii and data for group VIII compounds from Ref. 22.

Phos-phide	Structure type	R_X/R_{Me}	$d_{AA}/2R_{Me}$		$d_{AB}/2R_{Me}$		$d_{AC}/(R_{Me}+R_X)$		$d_{BC}/(R_{Me}+R_X)$	
			obs	calc	obs	calc	obs	calc	obs	calc
Ni_3P	Fe_3P	0.89	1.18	1.23	1.06	1.05	0.97	1.00	0.98	1.00
Fe_3P	»	0.87	1.18	1.22	1.06	1.04	0.98	1.00	0.99	1.00
Mn_3P	»	0.84	1.16	1.21	1.04	1.03	0.98	1.00	0.99	1.00
Ti_3P	Ti_3P	0.76	1.13	1.15	1.01	1.00	1.00	1.00	1.02	1.04
Nb_3P	»	0.75	1.13	1.15	1.02	1.00	1.00	1.00	1.06	1.05
Zr_3P	»	0.69	1.11	1.11	0.99	1.00	1.01	1.00	1.05	1.12

In Table 7 the averages of the four different distance types within a tetra-kaidecahedron are compared with those calculated. The calculation of these distances rests upon the following assumptions:

(a) A and B atoms are of the same element. C—A distances are always equal to $R_A + R_C$.
(b) The A—A distances are expanded uniformly, when the radius ratio $R_C/R_A > 0.53$.
(c) All A—B distances are equal to $2R_A$, when $R_C/R_A < 0.79$, and all B—C distances equal to $R_A + R_C$, when $R_C/R_A > 0.79$.

In view of the rather large spread within each distance type (Table 6) the agreement between calculated and observed distances is surprisingly good. The observed B—C distances are shorter than those calculated for Zr_3P, less so for Ti_3P. On closer inspection (see Table 6) it is observed that the prisms are in fact invariably more expanded in a direction parallel to the prism axis, resulting in shorter B—C distances. Nb_3P also shows the same tendency if we exclude the most distant B atom.

The existence of metal-nonmetal distances shorter than the radius sum in borides, silicides, and phosphides of the seventh and eighth group metals, observed earlier,[24] is illustrated in Table 7 through the inclusion of data for Mn_3P, Fe_3P, and Ni_3P. No such contraction is, however, found among the Ti_3P phases of the fourth and fifth group metals.

The similarities between the structure types Fe_3P, Ti_3P, α-V_3S, β-V_3S, tetragonal Ti_3Sb, and Cr_3Si have been discussed earlier.[4,22,25] It is also well-known that the number of superconductors among the compounds with the Cr_3Si (β-tungsten) type structure is exceptionally large and includes those with the highest known transition temperatures.[26] Thus a systematic investigation of the superconducting properties of the whole structure family might be valuable in clarifying the role of the crystal structure for the occurrence of superconductivity and the magnitude of the transition temperature.

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