ACTA CHEMICA SCANDINAVICA 27 (1967) 1773–1776

The Crystal Structure of TiP

PER-OLOF SNELL

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of TiP has been refined using single crystal X-ray methods. The space group is $P6_3/mmc$ and the unit cell dimensions are $a = 3.499$ Å and $c = 11.700$ Å. Four titanium atoms are situated in 4(*f*) with $z = 0.1170$ while the phosphorus atoms occupy the 2(*a*) and 2(*d*) positions. The crystal used for the structure refinement was grown from an iodine-containing gas phase in a temperature gradient.

In the course of a study of the Ti—P system [1] single crystals of TiP were obtained. The structure was previously determined by Schönberg [2] on the basis of X-ray powder diffraction data. However, it was decided to redetermine the structure using more accurate techniques. In particular it was thought desirable to obtain accurate P—Ti distances for the two nonequivalent phosphorus positions. These distances were stated by Schönberg [2] to be of equal length. The results given below show that this is not in fact the case.

EXPERIMENTAL

Preparation. Phosphide samples were prepared from titanium turnings (claimed purity 99.8 %, less than 0.07 % oxygen) and red phosphorus (better than 99 %). Mixtures of these elements were sealed off in evacuated silica capsules and heated at 850°C for 10 days. Because of the slow reaction rate, the material was crushed, pressed to pellets and reheated at the same temperature for another 10 days. The reaction product, containing only TiP, was heat treated at 550°C for 14 days with the addition of phosphorus. A black powder of TiP_2 was obtained in this way. Samples of TiP_2 were heat treated at temperatures between 500°C and 900°C. Phosphorus was evolved at around 650°C corresponding to the $TiP_2 \rightarrow TiP$ decomposition.

Well formed crystals of TiP were obtained by a chemical transport reaction with TiP_2 as the starting material. The crystal used for the structure refinement was grown from an iodine-containing gas phase in a temperature gradient. It was, however, found possible to transport TiP in the absence of iodine. It is difficult to decide which transport agent is responsible for the process. The fact that the evaporation rate of titanium in closed tubes is much larger than the sublimation in a continuously evacuated system has been taken as a proof that titanium migrates with the aid of a transport reaction in a temperature gradient. Schäfer [3] proposes that chlorine initially present from the preparation of titanium, may play a role.

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

Program	*Authors*
Leat squares refinement of unit-cell dimensions.	J. Tegenfeldt, Uppsala, Sweden.
Lorentz-polarization corrections	A. Zalkin, Berkeley, U.S.A., modified by R. Liminga and J.-O. Lundgren, 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.

X-Ray methods. Powder photographs were recorded in a Guinier-Hägg type focussing camera with strictly monochromatic Cu$K\alpha_1$ radiation (λ = 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 lattice parameters of TiP given in Table 2 are slightly larger than those given by Schönberg.[2]

Table 2. Final structure data for TiP.

Space group $P6_3/mmc$; Z = 4.

a = 3.499 Å $\quad \sigma(a)$ = 0.001 Å
c = 11.700 Å $\quad \sigma(c)$ = 0.006 Å

Atom	Position	x	y	z	$\sigma(z)$	B Å^2	$\sigma(B)$
Ti_I	4(f)	—	—	0.1170	0.0002	0.24	0.03
P_I	2(a)	—	—	—	—	0.55	0.09
P_{II}	2(d)	—	—	—	—	0.46	0.08

Frequent examples of twinning were encountered and the fragment used for the structure refinement was cut from a larger crystal. Due to the small size and/or perfection of the crystal the spots on ordinary Weissenberg photographs were extremely small and visual estimation of the intensities was difficult. The diffraction patterns were therefore recorded in a Wiebenga integrating camera. Intensities for 90 independent ($h0l$) reflections were recorded with Zr-filtered Mo$K\alpha$ radiation. The multiple-film method was employed with thin iron foils between successive films. The integrated intensities were measured photometrically.

STRUCTURE DETERMINATION

In the calculations of structure factors, atomic scattering factors, including the real part of the dispersion correction, were interpolated from the values listed in *International Tables*.[4]

A full-matrix least-squares refinement of the positional parameter, three isotropic temperature factors and one scale factor was finally made. Following

a suggestion by Cruickshank *et al.*[5] a weighting scheme according to the formula $w = 1/(a + |F_o| + c\,|F_o|^2)$ was employed with the constants $a = 35.0$ and $c = 0.012$. The refinement was terminated after five cycles. The largest shifts in the parameters were then less than 0.005 % of the standard deviations, and the R-value for the reflections was 0.085. The z-parameter obtained in this refinement ($z = 0.1170$) differs significantly from the value $z = 1/8$ given by Schönberg.[2] For details of the computer and the programs used, see Table 1.

DESCRIPTION OF THE TiP STRUCTURE

The monophosphides of the fourth group transition metals all crystallize with the TiP type structure (a NaCl-type ZrP phase also occurs). If the projection of the positions on the basal plane are designated by A, B, and C this structure may be described as an AABBAA. . . stacking of close-packed metal layers. The corresponding phosphorus atom sequence in ACBCACBC . . ., a mixture of the stacking in cubic and hexagonal close-packing. The two non-equivalent phosphorus atoms are situated in octahedral holes between A and B layers and trigonal prismatic holes between B and B layers (Fig. 1). The TiP structure may thus be considered from two viewpoints either as a NaCl—WC mixed type or a NiAs transposition type. The octrahedral P—Ti distances are 2.44 Å, while the trigonal prismatic P—Ti distances are 2.55 Å. The octahedral P—Ti distances are thus 0.11 Å shorter than the sum of the Goldschmidt metal radius for 12-coordination (1.45 Å) and the tetrahedral covalent radius of phosphorus (1.10 Å). The trigonal prism is somewhat distorted, the Ti—Ti distances in the triangular faces being 3.50 Å while those parallel to the prism axis are 3.11 Å. The octahedron is much less distorted, the Ti—Ti distances being 3.50 and 3.40 Å, respectively. The present result is in agreement with

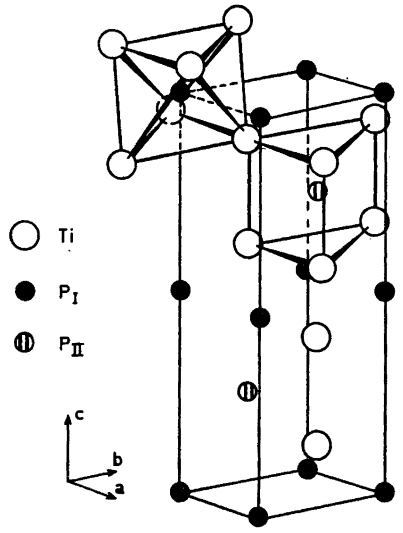

Fig. 1. The crystal structure of TiP.

Table 3. Interatomic distances and standard deviations (Å units) in TiP. Distances shorter than 4 Å listed.

Ti_I	— 3 P_I	2.440 ± 0.001	P_I	— 6 Ti_I	2.440 ± 0.001
	— 3 P_{II}	2.550 ± 0.002		— 6 P_I	3.499 ± 0.001
	— 1 Ti_I	3.112 ± 0.005		— 6 P_{II}	3.555 ± 0.001
	— 3 Ti_I	3.402 ± 0.004			
	— 6 Ti_I	3.499 ± 0.001	P_{II}	— 6 Ti_I	2.550 ± 0.002
				— 6 P_{II}	3.499 ± 0.001
				— 6 P_I	3.555 ± 0.001

the situation in the isomorphous HfP [6] and TiAs.[7] A similar situtation is also apparent in the isostructural H-phases, for instance Ti_2AlN,[8] where the larger Al atoms occupy the trigonal prismatic holes and the smaller N atoms fill the octahedral positions. There is no evidence that β-ZrP is different from the foregoing phases. Consequently, the interatomic distances for this phase given by Irani and Gingerich [9] must be questioned.

Acknowledgements. I wish to thank Professor G. Hägg for his kind interest and for all facilities put at my disposal.

I also want to thank Drs. T. Lundström and S. Rundqvist for valuable discussions and advice.

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

REFERENCES

1. Lundström, T. and Snell, P.-O. *Acta Chem. Scand.* **21** (1967) 1343.
2. Schönberg, N. *Acta Chem. Scand.* **8** (1954) 226.
3. Schäfer, H. *Chemical Transport Reactions*, Academic, New York 1964.
4. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
5. Cruickshank, D. W. J., Philling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, Pergamon, Oxford 1962, p. 32.
6. Jeitschko, W. and Nowotny, H. *Monatsh.* **93** (1962) 1107.
7. Lukaszewicz, K. and Trzebiatowski, W. *Bull. Acad. Polon. Sci. Classe III* **2** (1954) 277.
8. Jeitschko, W., Nowotny, H. and Benesovsky, F. *Monatsh.* **94** (1963) 1198.
9. Irani, K. S. and Gingerich, K. A. *J. Phys. Chem. Solids* **24** (1963) 1153.

Received March 22, 1967.