

Ti₇P₄ – Crystal Structure Refinement, and Structural Relationship with Ti₁₁CuP₈, Nb₈P₅ and Some Other Compounds

WILDER CARRILLO-CABRERA

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of Ti₇P₄ containing 2.1 atom-% copper has been refined using X-ray single-crystal diffractometry. The symmetry is monoclinic, space group *C2/m*, with lattice parameters: $a = 14.474(4)$ Å, $b = 3.4094(3)$ Å, $c = 13.616(2)$ Å and $\beta = 104.597(16)^\circ$. Ti₇P₄ is isotypic with Nb₇P₄. The refinement indicates a partial substitution of copper for titanium in the M(4) position. The environment of the M(4) atoms has a great similarity to that of the copper atoms in TiCuSi and Zr₃Cu₄Si₄. The structural relationships between Ti₇P₄ and some similar silicides, arsenides and phosphides are described.

Work at this institute has established the existence of a series of compounds with composition M₇X₄ isostructural with Nb₇P₄ in the binary Nb–As, Nb–P, Ta–P and Ti–P systems.^{1–4} There is also evidence for the occurrence of an Nb₇P₄ type compound in the Hf–As system.⁵ Crystals of Ti₇P₄ and other titanium-rich phosphides in ternary Ti–Cu–P samples were found to contain only a few atomic percent copper in solution.⁴ The recent structure determination of the Ti₁₁CuP₈ phase⁶ has stimulated interest in the detailed crystal structures of the other titanium phosphides containing copper. In the present paper the results of the structure refinement of Ti_{7–x}Cu_xP₄ with $x = 0.23$ are reported.

EXPERIMENTAL

Preparation. A copper-rich ternary alloy of nominal composition Ti_{0.02}Cu_{0.97}P_{0.01} (approx. 2.5 g) was prepared⁷ by initially reacting copper (Outokumpu Oy, Pori, Finland; as analyzed better than 99.99 %) and red phosphorus (Kebo, Stock-

holm, Sweden; better than 99 %) in an evacuated silica ampoule at 800 °C for three days and subsequently melting the reaction products together with lumps of titanium (Koch-Light Laboratories, Colnbrook, England; claimed purity 99.95 %) in a cold-crucible induction furnace. The sample was inhomogeneous even after annealing at 800 °C for 12 days. Small metallic crystals of (Ti,Cu)₇P₄, α -Ti₅P₃, (Ti,Cu)₄P₉ and β -(Ti,Cu)₅P₃ were isolated by dissolving the copper matrix in nitric acid.⁴

It was found that all the (Ti,Cu)₇P₄ crystals examined were twinned (with (001) as twinning plane). Even after crushing the crystals into smaller fragments it was not possible to select any which were not twinned. Nevertheless, the ratio of the volume of the smaller twin to the larger could be decreased. A crystal with a small satellite in the twin orientation was used for intensity measurements. The crystal was needle-shaped (the long axis coincident with the *b* axis of the unit cell) with the approximate dimensions 20 × 20 × 130 μm. Only the (100) and (001) faces were well-developed.

X-Ray diffraction measurements and data reduction. The single-crystal intensity data were collected using a Nonius CAD 4-F automatic diffractometer, controlled by a PDP 8/A computer. The ω - 2θ scan technique was used and reflections from one quarter of the reciprocal sphere were recorded to a maximum in 2θ of 86°. The cell dimensions of the crystal investigated were determined by least-squares refinement of the averages, θ_i , of the setting angles of 24 Friedel pairs of reflections with $15^\circ < 2\theta_i < 50^\circ$. MoK α radiation ($\lambda = 0.71069$ Å) was used for this measurement as well as for the intensity data collection. The intensities were corrected for Lorentz, polarization and absorption effects. Absorption correction was carried out using the Gaussian grid method and a linear absorption coefficient of 97.4 cm⁻¹ (calculated with mass absorption coefficients from Ref. 8, assuming two atomic percent

copper in the crystal). The minimum and maximum transmission factors obtained were 0.778 and 0.856. Correction for absorption in the smaller twin individual could not be applied. The systematic error arising was, however, considered to be negligible due to the small size and low absorption. In total, 2671 reflections were recorded, of which 1979 displayed positive intensities. Due to the twin type the $(0kl)$ reflections were completely overlapped by the $(0\bar{k}l)$ reflections of the smaller component crystal. All 57 $(0kl)$ reflections were used in the refinement, however, with a separate scale factor. From the two scale factors the ratio of the intensities from the main and "satellite" twin crystal respectively was found to be approximately 5:1. In total 150 reflections were deleted due to overlap with non-equivalent reflections from the smaller twin crystal.

Calculations. All calculations were performed with the computers NORD 100 and IBM 1800 using a system of programs described by Lundgren.⁹

STRUCTURE ANALYSIS AND RESULTS

The preliminary data obtained from Weissenberg films indicated a *C*-centred monoclinic cell. The conditions for (hkl) reflections were $h+k=2n$, which is consistent with the space groups *C2*, *Cm* or *C2/m*. The centrosymmetric *C2/m* (No. 12) space group was chosen and finally confirmed in the refinement.

The structure was refined using a full-matrix least-squares program⁹ and the atomic coordi-

nates² of Nb_7P_4 as initial values for the positional parameters. The quantity minimized was $\sum w(|F_o^2| - k^2|F_c^2|)^2$. Each reflection was assigned a weight w given by eqn. (1), where σ_c is the standard deviation

$$w^{-1} = [\sigma_c(F_o^2)]^2 + (p|F_o^2|)^2 \quad (1)$$

of F_o^2 , based on counting statistics, and p and empirical parameter, chosen to obtain a satisfactory weight analysis (p was 0.036 in the final refinement). The agreement indices are defined in eqns. (2) and (3), where F_o^2 has been multiplied by

$$R(F^2) = \Sigma(|F_o^2| - |F_c^2|) / \Sigma|F_o^2| \quad (2)$$

$$R_w(F^2) = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2} \quad (3)$$

$1/k^2$. Complex neutral-atom scattering factors were used.⁸ Extinction effects were hardly discernible and thus no correction was applied. Initially, the following parameters were refined: 2 scale factors, 20 positional parameters, and 12 isotropic temperature factors. The refinement on F^2 , based on 1829 positive reflections, converged rapidly, and the agreement factors obtained were:

$$R(F^2) = 0.130, R_w(F^2) = 0.131 \text{ and } R(F) = 0.126$$

The possibility of Cu/Ti substitution was then examined. Following the principle of good space filling, the smaller metal atoms (Cu) should pref-

Table 1. Structure data for $\text{Ti}_{6.77}\text{Cu}_{0.23}\text{P}_4$ from refinement based on F^2 . Space group *C2/m* (No. 12), $Z=4$. Standard deviations within parentheses. Cell dimensions: $a=14.474(4)$ Å, $b=3.4094(3)$ Å, $c=13.616(2)$ Å and $\beta=104.597(16)^\circ$. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{13}hla^*c^*)]$; $U_{12}=U_{23}=0$.

Atom	Position	Positional parameters			$U_{ij} \times 10^4$ (Å ²)				B (Å ²)
		x	y	z	U_{11}	U_{22}	U_{33}	U_{13}	
Ti(1)	2(a)	0	0	0	—	—	—	—	0.27(2)
Ti(2)	2(d)	0	1/2	1/2	—	—	—	—	0.27(2)
Ti(3)	4(i)	0.42787(10)	0	0.82790(11)	64(5)	14(6)	60(5)	11(4)	(0.39(2)) ^b
M(4) ^a	4(i)	0.19672(9)	0	0.31057(11)	59(5)	44(6)	91(5)	10(4)	(0.52(2)) ^b
Ti(5)	4(i)	0.20654(10)	0	0.79365(10)	—	—	—	—	0.33(2)
Ti(6)	4(i)	0.33944(9)	0	0.03274(10)	—	—	—	—	0.33(2)
Ti(7)	4(i)	0.00261(9)	0	0.66348(10)	47(5)	20(6)	38(5)	3(4)	(0.29(2)) ^b
Ti(8)	4(i)	0.17794(9)	0	0.54059(10)	—	—	—	—	0.28(2)
P(1)	4(i)	0.17847(14)	0	0.10806(15)	—	—	—	—	0.34(3)
P(2)	4(i)	0.37191(14)	0	0.60404(15)	62(8)	20(9)	42(7)	7(6)	(0.35(3)) ^b
P(3)	4(i)	0.36957(14)	0	0.34190(15)	54(8)	13(8)	35(7)	0(6)	(0.31(3)) ^b
P(4)	4(i)	0.06097(14)	0	0.84898(15)	71(8)	32(9)	20(7)	11(6)	(0.31(3)) ^b

^a M(4) = 0.77(1)Ti + 0.23(1)Cu. ^b Temperature factor from refinement assuming only isotropic thermal vibrations.

erentially occupy the positions which have small coordination numbers *i.e.* M(1), M(2) and M(4). Only in the M(4) site was a significant Cu/Ti substitution found. The least-squares refinement on F^2 gave an occupancy of 0.386 ($\sigma=0.007$) for Ti and 0.114 for Cu (reset), and the following R -values: $R(F^2)=0.124$, $R_w(F^2)=0.122$ and $R(F)=0.122$. A Hamilton R -factor significance test¹⁰ favoured the last model at the 99.5 % confidence level. Refinements under the assumption of Cu/Ti substitution in other metal positions with higher coordination numbers did not reveal any significant copper occupancy. A subsequent refinement with anisotropic temperature factors for all atoms showed that only six atoms could be regarded as anisotropic. The introduction of anisotropic factors for these six atoms led to somewhat improved agreement index. A Hamilton test¹⁰ favoured the model with the six anisotropic atoms at the 99.5 % confidence level. The final refinement on F^2 gave the following agreement values (1829 reflections):

$$R(F^2)=0.116, R_w(F^2)=0.115 \text{ and } R(F)=0.119.$$

The shifts in the final cycle were less than 0.03σ . The total number of parameters varied was 53 (two scale factors, one occupancy factor, 20 positional parameters and 30 temperature factors). The agreement factors for a refinement on F^2 omitting observations with $F_o^2 < 3\sigma(F_o^2)$ were (1126 reflections): $R(F^2)=0.081$, $R_w(F^2)=0.102$ and $R(F)=0.056$. The standard deviations were, however, on the average 17 % larger than those for the refinement of the more complete intensity material.

A normal probability ΔR -plot¹¹ after the final refinement displayed a very slightly S-shaped line with a slope of 0.92 and an intercept of -0.16 on the expected ΔR axis (no value fell outside the range $\pm 4\sigma$), indicating that the ΔR are randomly distributed with some underestimation of $\sigma(F^2)$. The standard deviation of an observation of unit weight,¹² S , was 1.19. A final difference Fourier map exhibited no electron density exceeding 4 % of a phosphorus peak in the F_o synthesis. The results from the final refinement are presented in Table 1. The interatomic distances are given in Table 2.

A list of observed and calculated structure factors can be obtained on request from the Institute of Chemistry, University of Uppsala, Sweden.

Table 2. Interatomic distances (Å) in Ti_{6.77}Cu_{0.23}P₄ less than 3.5 Å. Standard deviations within parentheses. M(4)=0.77 Ti + 0.23 Cu.

Ti(1)–2P(4)	2.434(2)	Ti(7)–P(4)	2.453(2)
–2P(1)	2.632(2)	–2P(2)	2.524(2)
–4Ti(3)	2.873(1)	–2P(3)	2.531(2)
–4Ti(6)	3.005(1)	–2Ti(2)	2.796(1)
–2Ti(1)	3.409(0)	–M(4)	2.995(2)
		–Ti(5)	3.037(2)
Ti(2)–2P(3)	2.480(2)	–2Ti(3)	3.211(2)
–2P(2)	2.602(2)	–Ti(8)	3.300(2)
–4Ti(7)	2.796(1)	–Ti(8)	3.374(2)
–4Ti(8)	3.022(1)	–2Ti(7)	3.409(0)
–2Ti(2)	3.409(0)		
		Ti(8)–2P(3)	2.548(2)
Ti(3)–2P(4)	2.534(2)	–2P(2)	2.562(2)
–2P(1)	2.591(2)	–P(2)	2.722(2)
–2M(4)	2.828(2)	–2M(4)	2.907(2)
–2Ti(1)	2.873(1)	–2Ti(2)	3.022(1)
–P(2)	2.950(2)	–2Ti(8)	3.105(2)
–Ti(5)	3.120(2)	–M(4)	3.211(2)
–2Ti(7)	3.211(2)	–Ti(7)	3.300(2)
–Ti(6)	3.349(2)	–Ti(5)	3.365(2)
–2Ti(3)	3.409(0)	–Ti(7)	3.374(2)
–Ti(6)	3.425(2)	–2Ti(8)	3.409(0)
M(4)–2P(2)	2.414(2)	P(1)–2Ti(5)	2.519(2)
–P(3)	2.430(2)	–2Ti(6)	2.529(2)
–P(1)	2.703(2)	–2Ti(3)	2.591(2)
–2Ti(5)	2.808(2)	–Ti(1)	2.632(2)
–2Ti(3)	2.828(2)	–M(4)	2.703(2)
–2Ti(8)	2.907(2)	–Ti(6)	2.773(2)
–Ti(7)	2.995(2)	–2P(1)	3.409(0)
–Ti(8)	3.211(2)		
–2M(4)	3.409(0)	P(2)–2M(4)	2.414(2)
		–2Ti(7)	2.524(2)
Ti(5)–P(4)	2.410(2)	–2Ti(8)	2.567(2)
–2P(1)	2.519(2)	–Ti(2)	2.602(2)
–2P(3)	2.550(2)	–Ti(8)	2.722(2)
–2M(4)	2.808(2)	–Ti(3)	2.950(2)
–Ti(7)	3.037(2)	–2P(2)	3.409(0)
–2Ti(6)	3.119(2)		
–Ti(3)	3.120(2)	P(3)–M(4)	2.430(2)
–Ti(6)	3.338(2)	–Ti(2)	2.480(2)
–Ti(8)	3.365(2)	–2Ti(7)	2.531(2)
–2Ti(5)	3.409(0)	–2Ti(8)	2.548(2)
		–2Ti(5)	2.550(2)
Ti(6)–2P(1)	2.529(2)	–P(3)	3.409(0)
–2P(4)	2.532(2)	–2P(4)	3.463(2)
–P(1)	2.773(2)		
–2Ti(1)	3.005(1)	P(4)–Ti(5)	2.410(2)
–2Ti(6)	3.040(2)	–Ti(1)	2.434(2)
–2Ti(5)	3.119(2)	–Ti(7)	2.453(2)
–Ti(5)	3.338(2)	–2Ti(6)	2.532(2)
–Ti(3)	3.349(2)	–2Ti(3)	2.534(2)
–2Ti(6)	3.409(0)	–2P(4)	3.409(0)
–Ti(3)	3.425(2)	–2P(3)	3.463(2)

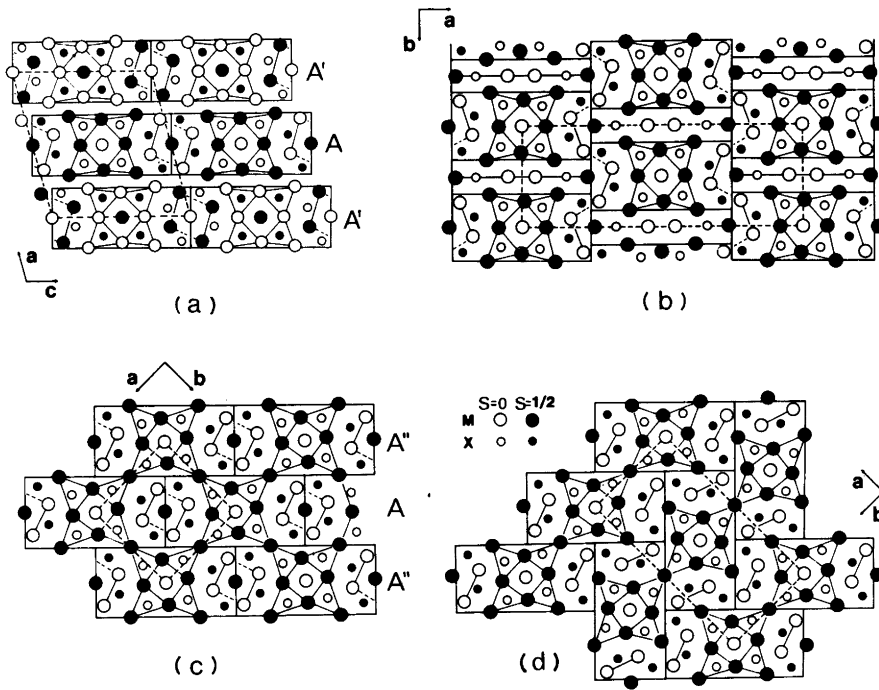


Fig. 2. Comparison among the structures of (a) Ti_7P_4 , (b) Nb_8P_5 , (c) V_3As_2 and (d) $Ti_{11}CuP_8$ as viewed along the short axis.

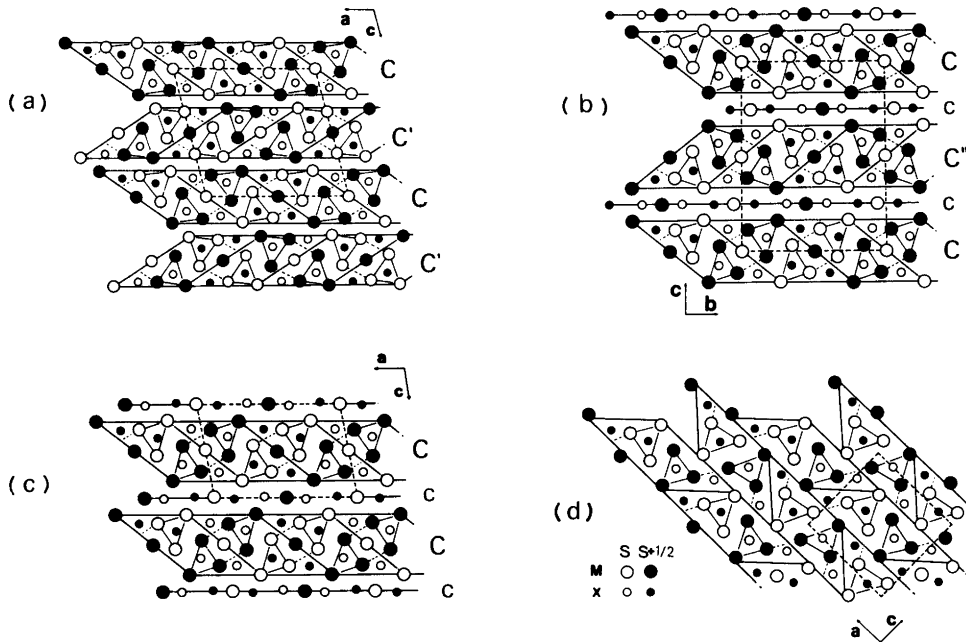


Fig. 3. Relationship between the structures of (a) Ti_7P_4 ($s=0$), (b) Nb_4As_3 ($s=0$), (c) Cr_4As_3 ($s=0$) and (d) Hf_3P_2 ($s=1/4$) as viewed along the short axis.

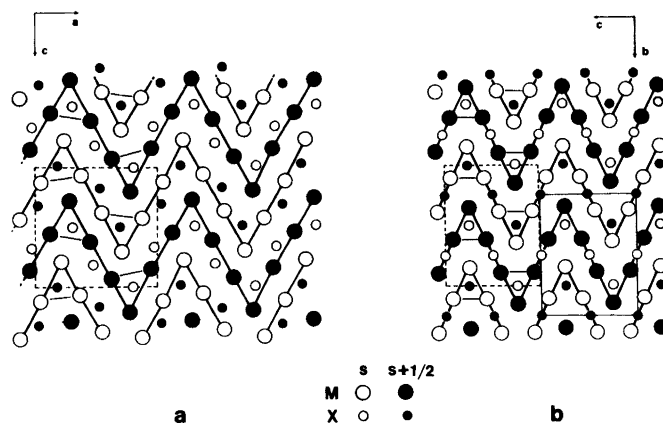
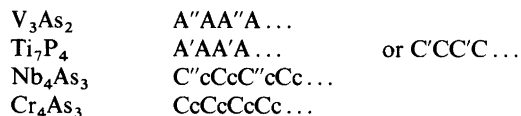


Fig. 4. Comparison of the structure of (a) Hf_3P_2 ($s=1/4$) with (b) V_3AsC ($s=0$; filled Re_3B type) projected along the short axis.

similarity of the environment of $\text{M}(4)$ in Ti_7P_4 with that of copper in TiCuSi and $\text{Nb}_5\text{Cu}_4\text{Si}_4$. A star-like building block, consisting of a body-centred cubic metal unit with four triangular prisms linked to it, is also discernible in the structures of $\text{Nb}_5\text{Cu}_4\text{Si}_4$ and Ti_7P_4 . The sequence of star-like blocks in the $[\bar{1}10]$ direction of $\text{Nb}_5\text{Cu}_4\text{Si}_4$ is identical to that of the blocks in the a direction of Ti_7P_4 , as shown in Figs. 1a and 1b.

Examination of the manner of packing of the triangular prisms and/or body-centred metal units in the less metal-rich arsenides and phosphides V_3As_2 ,¹⁶ Nb_4As_3 ,¹⁷ Cr_4As_3 ,¹⁸ Nb_8P_5 ,¹⁹ $\text{Ti}_{11}\text{CuP}_8$ and Hf_3P_2 ²⁰ reveals resemblances with that in Ti_7P_4 . This is demonstrated in Figs. 2 and 3, where the structures are shown in projection along the short axis. To make the similarities evident the structure of Ti_7P_4 has been partitioned into slabs and described in two additional ways: as a sequence of slabs packed in the a direction (Fig. 2a, slabs type A) or c direction (Fig. 3a, slabs type C). A slab of type A is related to one of type A' by a center of symmetry and a slab of type C is related to one of type C' by an operation of a pseudo-reflection glide plane. When slabs of type A are allowed to share metal atoms the structure of V_3As_2 is obtained as illustrated in Fig. 2c, where a slab of type A is related to one of type A'' by a slip of $a/\sqrt{2}$ in the $[1\bar{1}0]$ direction. By stacking extra layers of atoms (type c) between the C slabs the structures of Nb_4As_3 (Fig. 3b, C and C'' slabs) and Cr_4As_3 (Fig. 3c, only C slabs) are obtained. A slab of type C is related to one of type C'' by a reflection operation.

Using the notations given, the four structures can be described by the stacking sequence of slabs, or slabs and atom layers:



The structures of $\text{Ti}_{11}\text{CuP}_8$ (Fig. 2d) and Nb_8P_5 (Fig. 2b) can be described as different arrangements of a rectangular block (fragment of the slab of type A) centred at sites of high point symmetry. In Nb_8P_5 the parallel blocks are tied together by segments of atoms to form thicker slabs, which are stacked in the a direction, and adjacent slabs are related by a glide reflection operation. Fragments of the C slabs can be used to describe the structure of Hf_3P_2 as illustrated in Fig. 3d, where the fragments are connected in another manner to form a new type of slabs stacked in the c direction. Adjacent slabs are also related by a glide reflection operation. It should be observed as well that the structure of Hf_3P_2 is related to that of V_3AsC ²¹ (filled Re_3B type²²). A comparison of Fig. 4a with Fig. 4b shows that the Hf_3P_2 structure can be regarded as a distortion of the filled Re_3B type.

The relationships between Hf_3P_2 , $\text{Ti}_{11}\text{CuP}_8$ and Nb_8P_5 , between V_3As_2 , $\text{Ti}_{11}\text{CuP}_8$ and $(\text{Ti,Cu})_{14}\text{P}_9$ ²³ (Zr_{14}P_9 type²⁴), and between $\beta\text{-V}_4\text{As}_3$ (Cr_4As_3 type) and $\alpha\text{-V}_4\text{As}_3$ (Nb_4As_3 type) have also been discussed in Refs. 6, 23 and 25, respectively, using other descriptions of the structures.

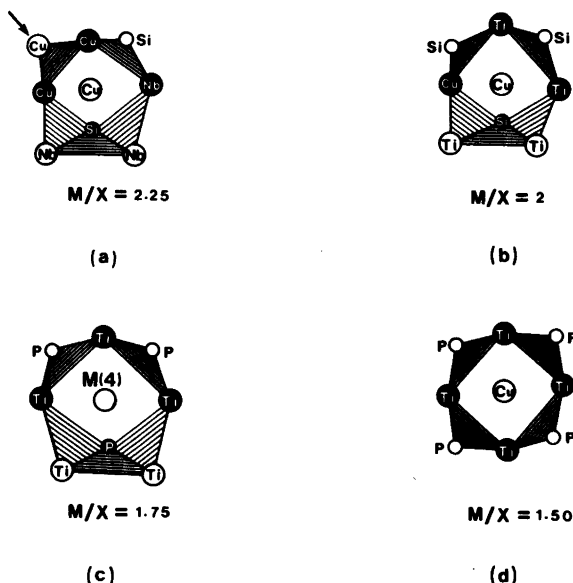


Fig. 5. Projections, as in Fig. 1, of the copper environment in the structures of (a) $\text{Nb}_5\text{Cu}_4\text{Si}_4$, (b) TiCuSi , (c) $\text{Ti}_{7-x}\text{Cu}_x\text{P}_4$ ($M(4)=0.77\text{ Ti}+0.23\text{ Cu}$) and (d) $\text{Ti}_{11}\text{CuP}_8$.

The changes of the atomic arrangement around the copper atom in some transition-metal silicides and phosphides, when the M/X ratio decreases from 2.25 ($\text{Nb}_5\text{Cu}_4\text{Si}_4$) to 1.50 ($\text{Ti}_{11}\text{CuP}_8$) are illustrated in Fig. 5 in projection along the short axis. The copper atom in these compounds has twelve nearest neighbours (only distances shorter than the length of the short axis are considered). Eight of these are situated at the corners of a quadrangular prism (*corner* atoms) with four further atoms outside the rectangular faces of the prism (*face* atoms). In $\text{Nb}_5\text{Cu}_4\text{Si}_4$ (Fig. 5a) each copper atom is surrounded by three silicon, four niobium and five copper atoms. The arrangement of atoms around copper in TiCuSi is shown in Fig. 5b. The main difference in nearest neighbour environment of copper in $\text{Nb}_5\text{Cu}_4\text{Si}_4$ and TiCuSi is the replacement of a *face* metal atom (indicated by an arrow in Fig. 5a) by a non-metal atom. Half of the *face* atoms and two of the *corner* atoms in TiCuSi are thus non-metals. The coordination of $M(4)$ in Ti_7P_4 (Fig. 5c) and that of copper in TiCuSi are very similar to that of copper in $\text{Zr}_3\text{Cu}_4\text{Si}_4$ ¹⁴ ($\text{Gd}_6\text{Cu}_8\text{Ge}_8$ type²⁶). The difference in environment of copper in these phases is the number of small metal neighbours, being three in $\text{Zr}_3\text{Cu}_4\text{Si}_4$, two in TiCuSi and none in Ti_7P_4 . In the metal poorer phase $\text{Ti}_{11}\text{CuP}_8$

the coordination polyhedron of the copper atom (Fig. 5d) is more regular than that of $M(4)$ in Ti_7P_4 . All *corner* atoms are metals and all *face* atoms are non-metals. The difference between the environment of $M(4)$ in Ti_7P_4 and that of copper in $\text{Ti}_{11}\text{CuP}_8$ can be regarded as an interchange between a *face* metal atom and a *corner* non-metal atom. The slightly distorted capped cubic environment also occurs in Ti_7P_4 around $M(1)$ and $M(2)$ (Fig. 1b), but dissolved copper atoms prefer the $M(4)$ site. However, in the $(\text{Ti,Cu})_{14}\text{P}_9$ phase,²³ with a M/X ratio of 1.56, the copper atoms populate a similar site to that of the copper atoms in $\text{Ti}_{11}\text{CuP}_8$.

The isotropic temperature factors of the atoms in Ti_7P_4 (Table 1) and the $\text{Ti}-\text{P}$ distances (Table 2) show no great differences from those found in $\alpha\text{-Ti}_5\text{P}_3$ ⁷ and $\text{Ti}_{11}\text{CuP}_8$.⁶ A closer look at Table 2 reveals that all the seven $\text{P}(4)-\text{Ti}$ distances are shorter than the sum of the tetrahedral covalent radius for phosphorus (1.10 Å) and the Goldschmidt metal radius (CN 12). The average distance between the $M(4)$ atom with $r_{M(4)}=0.77r_{\text{Ti}}+0.23r_{\text{Cu}}$ and its four phosphorus neighbours is 2.490 Å, which is slightly shorter than the radius sum of 2.51 Å (weighted radius for the $M(4)$ atoms used), while the average of the $M(4)-\text{Ti}$ distances (2.911 Å) is slightly larger than the radius sum (2.86 Å).

The Ti–Ti interatomic distances are somewhat shorter than the corresponding Nb–Nb distances in Nb₇P₄ owing to the greater size of the niobium atom as compared to titanium.

In the present study the copper content of the crystal investigated was found to be 2.1(1) atom-% (the composition of the crystal is thus Ti_{6.77}Cu_{0.23}P₄). There are apparent discrepancies in the cell parameters between the present ternary specimen (single-crystal data, Table 1; copper alloy with nominal Ti/P=2) and that in Ref. 4 (powder data, copper alloy with nominal Ti/P=3) with the same reported copper content. There might be significant differences in copper composition, however, since the ternary specimens had not been in complete equilibrium. Furthermore, the composition of the titanium-richer specimen (Ref. 4) was determined using an electron microprobe and the accuracy of the analysis was relatively low. The unit cell volumes of the above-mentioned ternary specimens are smaller than that reported⁴ for binary Ti₇P₄, which was measured on a titanium-rich sample. From the present data it is not possible, however, to establish unambiguously the range of homogeneity of Ti₇P₄ in the Ti–P and Ti–Cu–P systems.

Acknowledgements. The author thanks Doc. Torsten Lundström for his valuable advice and is also indebted to Prof. Stig Rundqvist for his interest in this work. The financial support granted by the Swedish Institute is gratefully acknowledged. This work has been supported by the Swedish Natural Science Research Council.

REFERENCES

1. Rundqvist, S., Carlsson, B. and Pontchour, C.-O. *Acta Chem. Scand.* 23 (1969) 2188.
2. Rundqvist, S. *Acta Chem. Scand.* 20 (1966) 2427.
3. Björkegren, J. and Andersson, Y. Institute of Chemistry, University of Uppsala, Uppsala 1976, UUIC-B18-53.
4. Carrillo-Cabrera, W. and Lundström, T. *Acta Chem. Scand.* A 33 (1979) 401.
5. Rundqvist, S. and Carlsson, B. *Acta Chem. Scand.* 22 (1968) 2395.
6. Carrillo-Cabrera, W. and Lundström, T. *Acta Chem. Scand.* A 35 (1981) 545.
7. Carrillo-Cabrera, W. and Lundström, T. *Acta Chem. Scand.* A 34 (1980) 415.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
9. Lundgren, J.-O., Ed., *Crystallographic Computer Programs*, Institute of Chemistry, University of Uppsala, Uppsala 1975, UUIC-B13-04-02.
10. Hamilton, W. C. *Acta Crystallogr.* 18 (1965) 502.
11. Abrahams, S. C. and Keve, K. T. *Acta Crystallogr. A* 27 (1971) 157.
12. Abrahams, S. C. *Acta Crystallogr. A* 25 (1969) 165.
13. Ganglberger, E. *Monatsh. Chem.* 99 (1968) 549.
14. Sprenger, H. J. *Less Common Met.* 34 (1974) 39.
15. Shoemaker, C. B. and Shoemaker, D. P. *Acta Crystallogr.* 18 (1965) 900.
16. Berger, R. *Acta Chem. Scand.* A 31 (1977) 287.
17. Carlsson, B. and Rundqvist, S. *Acta Chem. Scand.* 25 (1971) 1742.
18. Baurecht, H.-E., Boller, H. and Nowotny, H. *Monatsh. Chem.* 101 (1970) 1696.
19. Anugul, S., Pontchour, C.-O. and Rundqvist, *Acta Chem. Scand.* 27 (1973) 26.
20. Lundström, T. *Acta Chem. Scand.* 22 (1968) 2191.
21. Boller, H. and Nowotny, H. *Monatsh. Chem.* 98 (1967) 2127.
22. Boller, H. and Nowotny, H. *Monatsh. Chem.* 99 (1968) 721.
23. Carrillo-Cabrera, W. *Acta Chem. Scand.* A 36 (1982) 571.
24. Tergenius, L.-E., Nöling, B. I. and Lundström, T. *Acta Chem. Scand.* A 35 (1981) 693.
25. Berger, R. *Acta Chem. Scand.* A 28 (1974) 771.
26. Rieger, W. *Monatsh. Chem.* 101 (1970) 449.

Received September 10, 1981.