

Ti_{14-x}Cu_xP₉ ($x = 0.14$) – Crystal Structure Refinement, and Structural Relationship with Ti₁₁CuP₈ and V₃As₂

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The crystal structure of Ti_{14-x}Cu_xP₉ with $x = 0.14$ has been refined using X-ray single-crystal methods. The symmetry is orthorhombic (space group *Pnmm*). The cell dimensions of the crystal investigated were: $a = 15.509(4)$ Å, $b = 25.564(5)$ Å, $c = 3.4718(5)$ Å. The compound is isostructural with Zr₁₄P₉. relationship among the V₃As₂, Ti₁₁CuP₈ and Ti_{14-x}Cu_xP₉ structures is emphasized. A significant quantity of copper was found at the M(14) site. The capped cubic environment around M(14) is identical to that around the copper atom in Ti₁₁CuP₈.

Phase-analytical work on the Ti-Cu-P system¹ has revealed the occurrence of an orthorhombic phase with the formula M₁₄P₉ isostructural with Zr₁₄P₉.² Using electron micro-probe analysis the phase was found to contain small amounts of copper in solution. The purpose of this paper is to report the results of a single-crystal structure investigation of Ti_{14-x}Cu_xP₉ with $x = 0.14$.

EXPERIMENTAL

Preparation. Needle-shaped crystals of Ti_{14-x}Cu_xP₉ were formed on cooling a copper-rich ternary melt.^{1,3} The crystal used for the X-ray intensity measurement was picked from an inhomogeneous ternary sample (crystal A-1, sample A; Table 1). Crystals used for the refinements of the Ti₇P₄ and α -Ti₅P₃ structures^{3,4} were also selected from sample A.

Single-crystal diffractometry. The equipment and data collection procedure have been described previously.³ Up to $2\theta = 63.4^\circ$ one octant of the reciprocal lattice (h, k, l , positive) was measured. For $63.4^\circ < 2\theta < 68.0^\circ$ reflections with $0 \leq h \leq 24$, $0 \leq k \leq 40$ and $0 \leq l \leq 2$ were measured. 34 further

reflections (higher l -order reflections to some $h k 0$ and $h k 1$ strong reflections) with $5 \leq l \leq 8$ were also measured to improve the values of the temperature factors of the atoms. Instrumental stability and crystal setting were checked by remeasuring four test reflections at regular intervals. In total 2874 reflections were recorded, 37% of these had $F_o^2 > 3 \sigma(F_o^2)$. The crystal structure analysis was based on 1952 positive reflections. The cell dimensions of the crystal investigated were determined by least-squares refinement of the average of the setting angles, θ_i , of 33 Friedel pairs of reflections with $14^\circ < 2\theta_i < 50^\circ$. Graphite-monochromatized MoK α radiation ($\lambda = 0.71069$ Å) was employed for this measurement and for the intensity data collection.

The calculations were performed on IBM 1800 and NORD 100 computers. The intensity data were corrected for L_p and absorption (Gaussian grid technique) effects. The crystal had the approximate dimensions $13 \times 14 \times 254$ μm . The transmission varied between 0.829 and 0.913. The linear absorption coefficient (89.7 cm^{-1}) was calculated using the mass absorption coefficients given in Ref. 5, assuming 0.6 atomic percent copper in the crystal. The crystallographic programs used are described in Ref. 6.

CELL DIMENSION DETERMINATION

The cell dimensions of the Ti_{14-x}Cu_xP₉ phase in two ternary samples are given in Table 1. X-Ray single-crystal diffraction (as described above for crystal A-1) was used to determine the cell dimensions of crystal B-1. Sample A is deficient in phosphorus and sample B contains an excess of phosphorus. The samples were, however, inhomogeneous and thus the data of the powder (obtained by crushing aggregates of crystals) and single crystal specimens

Table 1. Unit cell dimensions for $Ti_{14-x}Cu_xP_9$ in Ti–Cu–P alloys as measured on single crystal and powder specimens. Standard deviations in parentheses. Sample B: high-frequency melted. Sample A: high-frequency melted and annealed at 800 °C for 12d.

Sample (nominal Ti/P)	Specimen	Copper content (at %)	Unit cell data				Ref.
			<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>U</i> (Å ³)	
B(Ti/P = 1.50)	Crystal B-1	0.76(11)	15.515(2)	25.568(4)	3.4816(3)	1381.1(3)	This work
A(Ti/P = 2.00)	Crystal A-1	0.60(6)	15.509(4)	25.564(5)	3.4718(5)	1376.5(5)	This work
	Powder A-2	n.d. ^a	15.529(1)	25.602(2)	3.4796(2)	1383.4(2)	1

^aThe result given in Ref. 1 was measured on a crystal that did not belong to A-2.

in Table 1 are representative for parts of the samples only. Table 1 shows that $Ti_{14-x}Cu_xP_9$ has a range of homogeneity.

STRUCTURE REFINEMENT

Preliminary Weissenberg photographs obtained from rotation of crystals around the *c* axis showed systematic absences for (*h* 0 *l*) and (0 *k* *l*) reflections corresponding to the space group *Pnmm* or *Pnn2*. The centrosymmetric *Pnmm* (No. 58) was initially adopted as the space group and confirmed in the refinement.

The structure was refined on F^2 using a full-matrix least-squares program⁶ and the atomic coordinates of $Zr_{14}P_9$.² The atomic scattering factors, including anomalous dispersion corrections, were taken from Ref. 5. Extinction effects were hardly discernible and thus no correction was applied.

The first refinement converged satisfactorily, but it was noted that the isotropic temperature factor for M(14), which has a low coordination number, was significantly lower than those for the other positions. This indicated a partial occupancy by copper in that position. The Cu/Ti substitution in the M(14) site was then examined. The least-squares refinement yielded a reasonable isotropic temperature factor for M(14) and gave an occupancy of 73(3) % for titanium and 27(3) % for copper (reset). The weighted R_w -value dropped from 0.1004 [$R(F^2) = 0.1388$] to 0.0978 [$R(F^2) = 0.1374$]. A significance test⁷ favoured the last model at the 99.5 % confidence level. Refinement under the assumption of substitution of copper for titanium in the other low coordinated site, 2(a), did not reveal any significant substitution. At this stage of the refinement the possibility of vacancies in the phosphorus sites with

low coordination number, P(1)–P(4), was tested. Only the occupancy of P(3) was found to decrease and was refined to 95.3 % ($\sigma = 1.5$ %). The isotropic temperature factor of P(3) decreased from 0.46 to 0.27 Å². The agreement factors obtained in the final refinement were (1952 reflections): $R_w(F^2) = 0.0976$, $R(F^2) = 0.1372$, and the standard deviation of an observation of unit weight,⁸ S , was 1.17. The agreement indices in the text are defined in Ref. 3. The function minimized in the refinements was $\sum w(|F_o^2| - |F_c^2|)^2$. The individual weight of a reflection, w , is defined as: $w^{-1} = [\sigma_c(F_o^2)]^2 + (p \cdot |F_o^2|)^2$, where σ_c is the standard deviation of F_o^2 , based on counting statistics, and p modifies the weight to obtain a satisfactory weight analysis ($p = 0.020$ in all the refinements).

The structure data from the final refinement are presented in Table 2 and the interatomic distances in Table 3. The following parameters were varied: one scale factor, 44 positional parameters, 24 isotropic temperature factors and two occupancy factors. The shifts in the final cycle were less than 0.002σ . No significant features could be found in a difference synthesis based on the final parameters. There were no positive or negative peaks exceeding 4 % of a phosphorus maximum in the corresponding F_o synthesis. The final fit between F_o^2 and F_c^2 was further examined by the ΔR normal probability plot.⁹ The plot was essentially linear with slope 0.95 and intercept -0.15 on the expected ΔR axis (four values fell outside the range $\pm 4\sigma$), indicating that the ΔR are random-normally distributed.

The R values for a refinement omitting reflections with $F_o^2 < 3\sigma(F_o^2)$ were (1070 reflections): $R_w(F^2) = 0.0856$, $R(F^2) = 0.0927$. The standard deviations were, however, on the average 24 % larger than those for the refinement using the more complete material.

Table 2. Final structural data for $Ti_{13.86}Cu_{0.14}P_{8.95}$ from refinement based on F^2 . Space group $Pnmn$ (No. 58), $a = 15.509(4)$ Å, $b = 25.564(5)$ Å, $c = 3.4718(5)$ Å; $U = 1376.5(5)$ Å³; $Z = 4$. Standard deviations are given in parentheses.

Atom	Position	Positional parameters			B (Å ²)
		x	y	z	
Ti(1)	4g	0.05053(15)	0.57814(10)	0	0.35(4)
Ti(2)	4g	0.09966(16)	0.10455(10)	0	0.33(4)
Ti(3)	4g	0.11744(16)	0.75592(10)	0	0.39(4)
Ti(4)	4g	0.13333(16)	0.46936(9)	0	0.34(4)
Ti(5)	4g	0.13822(16)	0.35314(10)	0	0.36(4)
Ti(6)	4g	0.19941(16)	0.99089(9)	0	0.34(4)
Ti(7)	4g	0.20206(16)	0.85716(10)	0	0.44(4)
Ti(8)	4g	0.24642(15)	0.58313(9)	0	0.29(4)
Ti(9)	4g	0.26794(16)	0.18783(9)	0	0.36(4)
Ti(10)	4g	0.33300(15)	0.76277(10)	0	0.30(4)
Ti(11)	4g	0.43146(15)	0.42575(10)	0	0.40(4)
Ti(12)	4g	0.48069(16)	0.17682(9)	0	0.29(4)
Ti(13)	4g	0.48780(16)	0.69692(10)	0	0.36(4)
M(14) ^a	2d	0	1/2	1/2	0.42(7)
Ti(15)	2a	0	0	0	0.38(6)
P(1)	4g	0.13255(24)	0.65708(14)	0	0.37(6)
P(2)	4g	0.34140(23)	0.66558(13)	0	0.26(6)
P(3) ^b	4g	0.04808(23)	0.85831(14)	0	0.27(9)
P(4)	4g	0.26699(22)	0.42227(14)	0	0.38(6)
P(5)	4g	0.27447(24)	0.28585(14)	0	0.32(6)
P(6)	4g	0.04757(23)	0.26705(14)	0	0.38(6)
P(7)	4g	0.43674(23)	0.90775(13)	0	0.33(6)
P(8)	4g	0.34393(23)	0.03780(13)	0	0.27(5)
P(9)	4g	0.39708(24)	0.53245(14)	0	0.36(6)

^a M(14) = 0.73(3)Ti + 0.27(3) Cu. ^b Occupancy 0.963(15).

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

In a preliminary X-ray single-crystal study of $Ti_{14-x}Cu_xP_9$, a very small crystal (crystal B-1, approx. $8 \times 6 \times 188$ μm, sample B, Table 1) was investigated. Of the 2299 independent reflections

measured for $2\theta < 60^\circ$, only 25% had $F_o^2 > 3\sigma(F_o^2)$. This affected the refinement resulting in relatively high final R values and estimated standard deviations of the parameters. The final agreement factors for the refinement on F^2 were (1718 positive reflections): $R_w(F^2) = 0.132$, $R(F^2) = 0.221$ and $S = 0.97$. The refinement yielded an occupancy of 65(5)%

Table 3. Interatomic distances and standard deviations for $Ti_{13.86}Cu_{0.14}P_{8.95}$ (Å units). The distances listed are less than 3.48 Å. M(14) = 0.73 Ti + 0.27Cu.

Ti(1)–P(1)	2.385(4)	Ti(2)–P(3)	2.480(4)
–2P(7)	2.502(3)	–2P(2)	2.507(3)
–2P(8)	2.599(3)	–2P(9)	2.533(3)
–2M(14)	2.760(2)	–2Ti(8)	3.002(3)
–Ti(8)	3.041(3)	–Ti(15)	3.087(2)
–Ti(4)	3.063(3)	–2Ti(11)	3.228(3)
–Ti(4)	3.099(3)	–2Ti(13)	3.229(3)
–2Ti(12)	3.100(3)	–Ti(6)	3.292(3)
–Ti(5)	3.414(3)	–Ti(9)	3.368(3)
–2Ti(1)	3.472(0)	–2Ti(2)	3.472(0)

Table 3. Continued.

Ti(3) – 2P(5)	2.532(3)	Ti(8) – 2P(8)	2.514(3)
– P(1)	2.538(4)	– P(2)	2.571(4)
– P(6)	2.626(4)	– P(1)	2.587(4)
– P(3)	2.830(4)	– P(9)	2.672(4)
– Ti(7)	2.902(4)	– 2Ti(2)	3.002(3)
– 2Ti(13)	2.917(3)	– Ti(1)	3.041(3)
– 2Ti(9)	3.034(3)	– 2Ti(6)	3.041(3)
– 2Ti(12)	3.069(3)	– 2Ti(9)	3.198(3)
– Ti(10)	3.348(3)	– Ti(4)	3.396(3)
– 2Ti(3)	3.472(0)	– 2Ti(8)	3.472(0)
Ti(4) – P(4)	2.397(4)	Ti(9) – 2P(1)	2.452(3)
– 2P(8)	2.490(3)	– 2P(2)	2.492(3)
– 2P(7)	2.584(3)	– P(5)	2.508(4)
– 2M(14)	2.811(2)	– 2Ti(10)	3.022(3)
– Ti(5)	2.972(4)	– 2Ti(3)	3.034(3)
– Ti(1)	3.063(3)	– 2Ti(8)	3.198(3)
– Ti(1)	3.099(3)	– Ti(12)	3.312(4)
– 2Ti(6)	3.170(3)	– Ti(2)	3.368(3)
– Ti(8)	3.396(3)	– 2Ti(9)	3.472(0)
– 2Ti(4)	3.472(0)		
Ti(5) – 2P(7)	2.513(3)	Ti(10) – 2P(5)	2.478(3)
– P(6)	2.611(4)	– P(2)	2.488(4)
– P(4)	2.667(4)	– 2P(6)	2.541(3)
– P(5)	2.725(4)	– 2Ti(5)	2.924(3)
– 2Ti(10)	2.924(3)	– Ti(13)	2.932(3)
– Ti(4)	2.972(4)	– 2Ti(9)	3.022(3)
– 2Ti(7)	3.027(3)	– Ti(7)	3.154(3)
– 2Ti(12)	3.093(3)	– Ti(12)	3.276(3)
– Ti(1)	3.413(3)	– Ti(3)	3.348(3)
– 2Ti(5)	3.472(0)	– 2Ti(10)	3.472(0)
Ti(6) – 2P(4)	2.522(3)	Ti(11) – 2P(3)	2.467(3)
– 2P(9)	2.526(3)	– P(4)	2.552(4)
– P(8)	2.542(4)	– P(9)	2.779(4)
– 2Ti(8)	3.046(3)	– 2Ti(15)	2.783(2)
– Ti(15)	3.101(3)	– P(9)	2.866(4)
– 2Ti(11)	3.147(3)	– 2Ti(6)	3.147(3)
– 2Ti(4)	3.170(3)	– 2Ti(7)	3.221(3)
– Ti(2)	3.292(3)	– 2Ti(2)	3.228(3)
– Ti(7)	3.419(4)	– Ti(13)	3.377(4)
– 2Ti(6)	3.472(0)	– 2Ti(11)	3.472(0)
Ti(7) – P(3)	2.388(4)	Ti(12) – 2P(6)	2.480(3)
– 2P(4)	2.452(3)	– P(7)	2.513(4)
– 2P(5)	2.543(3)	– 2P(1)	2.520(3)
– Ti(3)	2.902(4)	– 2Ti(3)	3.069(3)
– 2Ti(5)	3.027(3)	– 2Ti(5)	3.093(3)
– Ti(10)	3.154(3)	– 2Ti(1)	3.100(3)
– 2Ti(11)	3.221(3)	– Ti(13)	3.265(3)
– Ti(6)	3.419(4)	– Ti(10)	3.276(3)
– 2Ti(7)	3.472(0)	– Ti(9)	3.312(4)
		– 2Ti(12)	3.472(0)

Table 3. Continued.

Ti(13)–P(2)	2.408(4)	P(4)–Ti(4)	2.397(4)
–2P(3)	2.425(4)	–2Ti(7)	2.452(3)
–2P(6)	2.555(3)	–2Ti(6)	2.522(3)
–2Ti(3)	2.917(3)	–Ti(11)	2.552(4)
–Ti(10)	2.932(3)	–Ti(5)	2.667(4)
–2Ti(2)	3.229(3)	–P(9)	3.465(5)
–Ti(12)	3.265(3)	–2P(4)	3.472(0)
–Ti(11)	3.377(4)		
–2Ti(13)	3.472(0)		
M(14)–2P(7)	2.554(3)	P(5)–2Ti(10)	2.478(3)
–2P(8)	2.606(4)	–Ti(9)	2.508(4)
–4Ti(1)	2.760(2)	–2Ti(3)	2.532(3)
–4Ti(4)	2.811(2)	–2Ti(7)	2.543(3)
–2M(14)	3.472(0)	–Ti(5)	2.725(4)
		–2P(5)	3.472(0)
Ti(15)–4P(9)	2.500(3)	P(6)–2Ti(12)	2.480(3)
–4Ti(11)	2.783(2)	–2Ti(10)	2.541(3)
–2Ti(2)	3.087(2)	–2Ti(13)	2.555(3)
–2Ti(6)	3.101(3)	–Ti(5)	2.611(4)
–2Ti(15)	3.472(0)	–Ti(3)	2.626(4)
		–P(1)	3.401(5)
		–2P(6)	3.472(0)
P(1)–Ti(1)	2.385(4)	P(7)–2Ti(1)	2.502(3)
–2Ti(9)	2.452(3)	–2Ti(5)	2.513(3)
–2Ti(12)	2.520(3)	–Ti(12)	2.513(4)
–Ti(3)	2.538(4)	–M(14)	2.554(3)
–Ti(8)	2.587(4)	–2Ti(4)	2.584(3)
–P(2)	3.246(5)	–2P(7)	3.472(0)
–P(6)	3.401(5)		
–2P(1)	3.472(0)	P(8)–2Ti(4)	2.490(3)
P(2)–Ti(3)	2.408(4)	–Ti(6)	2.513(3)
–Ti(10)	2.488(4)	–Ti(6)	2.542(4)
–2Ti(9)	2.492(3)	–2Ti(1)	2.599(3)
–2Ti(2)	2.507(3)	–M(14)	2.606(4)
–Ti(8)	2.571(4)	–2P(8)	3.472(0)
–P(1)	3.246(5)		
–2P(2)	3.472(0)	P(9)–2Ti(15)	2.500(3)
P(3)–Ti(7)	2.388(4)	–2Ti(6)	2.526(3)
–2Ti(13)	2.425(3)	–2Ti(2)	2.533(3)
–2Ti(11)	2.467(3)	–Ti(8)	2.672(4)
–Ti(2)	2.480(4)	–Ti(11)	2.779(4)
–Ti(3)	2.830(4)	–Ti(11)	2.866(4)
–2P(3)	3.472(0)	–P(4)	3.46(5)
		–P(9)	3.472(0)

for titanium and 35(5) % for copper in the M(14) site. No indication of any appreciable deviation from the ideal $M_{14}P_9$ formula was obtained from the refinement of the structure of this crystal (B-1) selected from a phosphorus-rich sample. The stand-

ard deviations of the parameters on the average were two times larger than those for the crystal A-1, in Table 2. Only one positional parameter differed by 4σ . For the other parameters the difference was less than 2σ (σ is the standard deviation of the

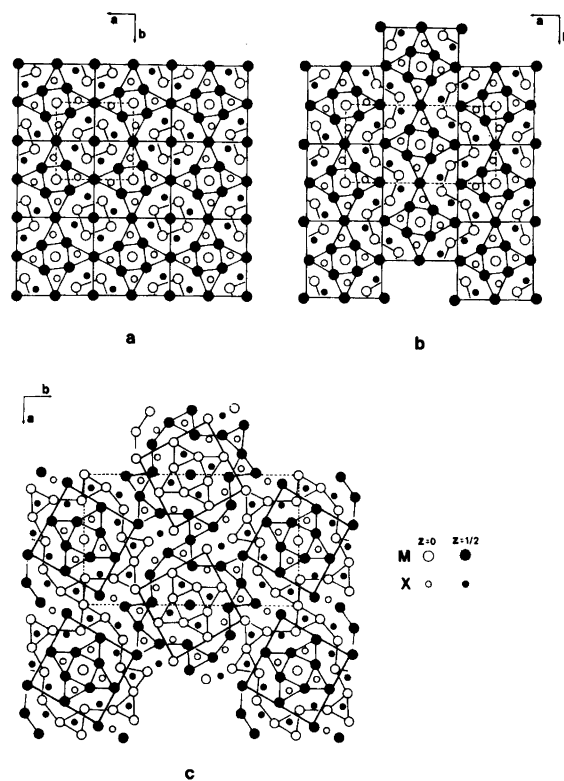


Fig. 1. Relationship between the structure of (a) V_3As_2 , (b) $Ti_{11}CuP_8$ and (c) $Ti_{14-x}Cu_xP_9$ ($Zr_{14}P_9$ type) as viewed along the c axis.

differences between the parameters for crystal B-1 and the corresponding ones for crystal A-1, in Table 2). Comparison of the interatomic distances gave similar differences, being no greater than 3σ .

DISCUSSION

The present single-crystal refinement confirms that $Ti_{14-x}Cu_xP_9$ is isostructural with $Zr_{14}P_9$.² The general structural features of the type have been described in Ref. 2. However, some additional comments, based on structural comparisons, are given here.

A projection of the structure along the c axis is shown in Fig. 1c. Examination of the structure reveals resemblances with those of V_3As_2 ,¹⁰ $Ti_{11}CuP_8$ ¹¹ and Nb_5P_3 ,¹² regarding the manner of packing of the triangular prisms of metals (which surround the non-metal atoms) and the metal body-centred unit as demonstrated in Figs. 1 and 2.

In both figures only the triangular prisms around the non-metals atoms, which have high coordination numbers (8 or 9), are indicated. Common structural fragments are also indicated to emphasize relationship and differences between the structures.

The V_3As_2 and $Ti_{11}CuP_8$ structure types are geometrically closely related. Both types can formally be described on the basis of different arrangements of a common sub-unit, which is also discernible in the more complex structure of $Ti_{14-x}Cu_xP_9$, as illustrated in Fig. 1. The sub-unit consists of one unit cell of the tetragonal V_3As_2 . The $Ti_{11}CuP_8$ structure can thus be derived from the V_3As_2 type through a glide reflection operation.

The $Ti_{14-x}Cu_xP_9$ structure (Fig. 2c) retains large fragments from $Ti_{11}CuP_8$ (Fig. 2a, block A) and Nb_5P_3 (Fig. 2b, block B), the latter represented by $\beta-(Ti,Cu)_5P_3$ in the Ti-Cu-P system.¹ The coordination polyhedra for the corresponding atoms within the common blocks (A or B) are thus similar.

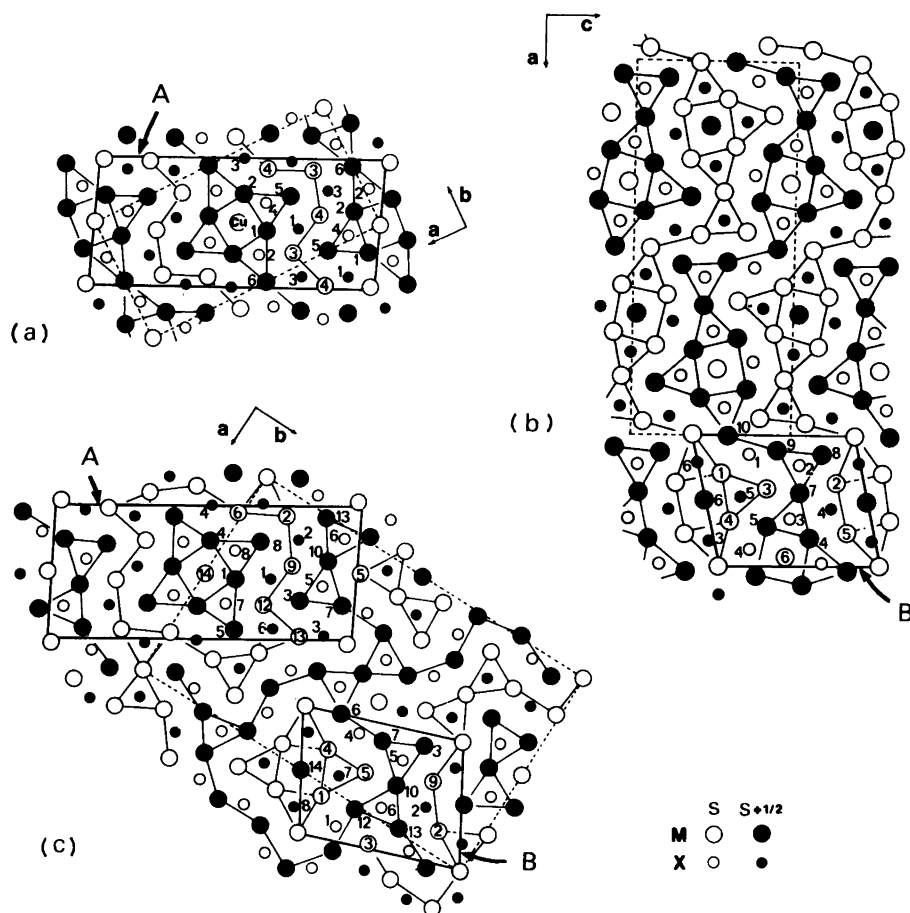


Fig. 2. Comparison among the structures of (a) $Ti_{11}CuP_8$ ($s=0$), (b) Nb_5P_3 ($s=1/4$) and (c) $Ti_{14-x}Cu_xP_9$ ($s=0$) as viewed along the short axis.

However, the environments of Ti(3) and Ti(6) in $Ti_{11}CuP_8$ and those of Nb(8) and Nb(9) in Nb_5P_3 have no counterpart in the structure of $Ti_{14-x}Cu_xP_9$.

The close similarity between $Ti_{11}CuP_8$ and $Ti_{14-x}Cu_xP_9$, which have slightly different compositions, is further substantiated by the fact that the copper atoms in both structures are accommodated in nearly identical crystallographic sites (Cu and M(14) in Figs. 2a and 2c, respectively). The coordination polyhedron around M(14) in $Ti_{14-x}Cu_xP_9$, as well as that around copper in $Ti_{11}CuP_8$, is a distorted capped cube which is situated at the center of the tetragonal sub-unit common to both structures (Figs. 1b and 1c).

Recently³ it has been found that 23% of the titanium in the M(4) site of Ti_7P_4 can be replaced

by copper. The arrangement of atoms (metals and non-metals) around M(4) in Ti_7P_4 is different from that around M(14) in $Ti_{14-x}Cu_xP_9$, but consists in both cases of eight titanium and four phosphorus atoms. The main difference between the atomic environments of copper in Ti_7P_4 , $Ti_{11}CuP_8$ and other compounds in similar systems has been discussed in Ref. 3. Contrary to what is observed in Ti_7P_4 for M(4), in $Ti_{14-x}Cu_xP_9$ the average distance between the M(14) atom and its eight titanium neighbours (2.79 Å) is shorter than the radius sum of 2.85 Å (Goldschmidt CN 12 metal radii and weighted radius $r_{M(14)} = 0.73r_{Ti} + 0.27r_{Cu}$ used) and the average of the M(14)–P distances (2.58 Å) is larger than the corresponding radius sum of 2.50 Å (tetrahedral covalent radius for

phosphorus used).

The isotropic temperature factors of the atoms in $Ti_{14-x}Cu_xP_9$ (Table 2) are similar to those found in $Ti_{11}CuP_8$, Ti_7P_4 and $\alpha-Ti_5P_3$.⁴ The interatomic distances in $Ti_{14-x}Cu_xP_9$ (Table 3) show a conspicuous feature which has also been observed for the structure of $Ti_{11}CuP_8$: most of the Ti–P distances (75 %) are shorter than the corresponding radius sum of 2.55 Å, whereas the Ti–Ti distances (with the exception of the two Ti(11)–Ti(15) distances of 2.78 Å) are longer than the radius sum of 2.90 Å. In the isostructural $Zr_{14}P_9$, however, about 42 % of the Zr–P distances are longer than the corresponding radius sum of 2.70 Å and twelve Zr–Zr distances are shorter than the radius sum of 3.20 Å.

The number of metal neighbours around the phosphorus atoms in $Ti_{14-x}Cu_xP_9$, as well as in $Zr_{14}P_9$, are seven for P(1)–P(4), eight for P(5)–P(8) and nine for P(9). Nevertheless, a closer examination of the interatomic distances in Table 3 reveals that the trigonal prism around P(3) is very distorted: the distance to one metal atom [Ti(3)] at a corner of this prism is very long (2.83 Å), but the other Ti–P(3) distances are shorter than the radius sum 2.55 Å. The coordination number of P(3) is thus 6(+1) rather than 7. This is also valid for P(3) in $Zr_{14}P_9$.

In the present study the copper content of the two crystals investigated were found to be practically the same (0.60(6) atom-% for A-1 and 0.76(11) atom-% for B-1). The cell volume of the crystal A-1 was, however, significantly smaller than that of the crystal B-1, which was selected from an alloy containing an excess of phosphorus (sample B). Only the short (*c*) axis of A-1 decreased, see Table 1. The decrease in volume (or short axis) might be interpreted in terms of phosphorus vacancies. The structure refinement supported this assumption: the occupancy for P(3) in crystal A-1 (Table 2) refined to 95.3 % ($\sigma = 1.5$ %) while the corresponding one in B-1 converged to 100 %. A comparison between the interatomic distances in the two crystals showed that the largest differences were associated with the atomic environment about P(3). The average of the P(3)–Ti distances was 0.007 Å smaller in the A-1 crystal than in B-1, and all the Ti–Ti distances within the Ti_6 prism surrounding P(3) were shorter in A-1 by amounts corresponding to one or two standard deviations of the differences between A-1 and B-1. It therefore seems likely that the vacancy model is correct and the composition

of the crystal A-1 should accordingly be $Ti_{13.86}Cu_{0.14}P_{8.95}$.

The ternary sample A was very inhomogeneous (it contained more than three phases) and specimens from different parts of the sample gave different cell parameters. It can be seen from Table 1 that the cell volume of A-2 powder is bigger than that of crystal A-1.

It has not been possible, as was mentioned in Ref. 1, to prepare a $Ti_{14}P_9$ phosphide in the binary Ti–P system.

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