

# Ternary Phosphide $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$ , Its Crystal Structure, and $RE_{m+n}(\text{Cu}_2\text{P}_3)_m(\text{Cu}_4\text{P}_2)_n$ Relationship with Other Rhombohedral Rare-Earth Copper Phosphides

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Crystals of the phosphide  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  ( $x = 0.41$ ,  $y = 0.50$ ) have been prepared by annealing pressed powders of the elements at  $800^\circ\text{C}$  for 2 weeks. The structure was determined by single-crystal methods: space group  $R\bar{3}m$  (No. 166),  $Z = 3$ ,  $a = 3.976(1)$  Å,  $c = 40.554(8)$  Å,  $R = 0.045$  for 243 independent reflections [ $F > 4\sigma(F)$ ]. The unit cell of  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  can be built from a close packing of Ho atoms and fragments of  $\text{Cu}_3\text{P}$ , with one of the fragments containing additional P atoms. It can be also considered as an intercalation of additional P atoms in the  $\text{YbCu}_{3-x}\text{P}_2$  structure (P. Klüfers, A. Mewis, and H. U. Schuster, *Z. Kristallogr.* 149, 211 (1979)). The  $RE_{m+n}(\text{Cu}_2\text{P}_3)_m(\text{Cu}_4\text{P}_2)_n$  relationship with other rare-earth copper phosphides, having similar structural characteristics is discussed. © 2000 Academic Press

**Key Words:** holmium copper phosphide; crystal structure; structural relationships.

## INTRODUCTION

Ternary phosphides have been under intensive investigation for the past few decades, and a lot of attention has been paid to the syntheses and characterization of new phases with rare-earth and  $3d$  elements (2). As a result, a number of compounds exhibiting a large structural variety have been synthesized. Many similarities as well as differences can be found between them in terms of compositions, building units, and packing characteristics. Introducing a new rare earth into the structure usually makes it possible to track steric effects, while substitution of  $3d$  metals reflects the dependence of the structure on the electronic nature of the elements. Many of the phosphides have been formed in the region of about 33 at.% of phosphorus and with less than 30 at.% of a rare earth, with the largest number of phases (with the ratio of metals to phosphorus around 2:1) being found in the nickel-containing systems (2).

Since a trigonal-prismatic coordination is characteristic of P atoms in the rare-earth transition metal phosphides with 26–36 at.% of P, the structures can be analyzed and the compositions can be determined on the basis of the stacking character of those trigonal prisms with P atoms inside (2). For the hexagonal structures, with all atoms forming two flat nets, the authors (2) suggested a general formula  $R_{m(m-1)/2}M_{(m+1)(m+2)/2}P_{m(m+1)/2}$ , where  $m$  is an integer and  $R$  and  $M$  correspond to the largest and medium-sized atoms, respectively. But depending on the stacking of the trigonal prisms and the positions of metal atoms, the hexagonal structures are divided into separate series with their own chemical formulas.

The above description is mainly applicable to the Fe-, Co-, or Ni-containing phosphides, while Cu phosphides, exhibiting rather a smaller structural and compositional variety, were not so well described. So, we have focused our interest on the copper compounds and during the investigation of the Ho–Cu–P system at  $800^\circ\text{C}$  two new compounds  $\sim\text{Ho}_2\text{Cu}_5\text{P}_3$  and  $\sim\text{HoCu}_5\text{P}_4$ , have been found (3). The composition and the crystal structure of the latter were determined by powder methods:  $\text{Ho}_3\text{Cu}_{8-y}\text{P}_8$  (space group  $R\bar{3}m$ ,  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  type,  $a = 3.974$  and  $c = 60.04$  Å) (4). The  $RE_3\text{Cu}_{8-y}\text{P}_8$  phosphides have been synthesized for other heavy rare earths (RE) and they all proved to be isostructural with  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$ . The  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  structure was rationalized in terms of the structural units found in other phosphides and their similarities were discussed in (4).

The powder pattern of the  $\sim\text{Ho}_2\text{Cu}_5\text{P}_3$  phosphide was similar to that of  $\text{Ho}_3\text{Cu}_{8-y}\text{P}_8$ , indicating a possible structural relationship between these two compounds; additionally their compositions were close. However, some differences in the X-ray patterns pointed out that  $\sim\text{Ho}_2\text{Cu}_5\text{P}_3$  must have its own structure. Single crystals of the phosphide have been prepared in order to solve the structure, to refine atomic and thermal parameters, and to check for atomic deficiencies. We have also tried to examine

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the structural features of the new phase and to define a crystal chemical rule to describe the rhombohedral rare-earth copper phosphides.

## EXPERIMENTAL AND STRUCTURE DETERMINATION

Starting materials were powders of holmium (ChemPur, 99.9%), copper (Heraeus 99.9%), and amorphous red phosphorus (Aldrich, 99%). The copper powder was reduced in a stream of hydrogen at 400°C for 4 hours and subsequently stored in an Ar-filled glove box. Weighing and handling of the samples were performed in the glove box as well. Powders of the elements at the initial composition Ho<sub>2</sub>Cu<sub>5</sub>P<sub>3</sub> with a total mass of 1 g were intimately mixed, pressed to a pellet under the pressure of 1500 kg using a 10-mm dial tool, and sealed in an evacuated silica tube. The Ho<sub>2</sub>Cu<sub>5</sub>P<sub>3</sub> sample was annealed at 800°C for 2 weeks and quenched in cold water. After annealing, a black powder containing small crystals with a metallic luster was obtained.

A single crystal with the shape of a regular rhombohedron was chosen for the X-ray structure investigation. The Laue method was used to determine its symmetry ( $\bar{3}m$ ) and suitability for the data collection. The lattice parameters  $a = 3.98 \text{ \AA}$  and  $c = 41.49 \text{ \AA}$  were derived from rotation and reciprocal lattice photography films. Examination of the 0- and 1-level reciprocal lattice pictures showed the existence of the reflections only with  $-h + k + l = 3n$ , which was a limiting condition for a rhombohedral unit cell in the hexagonal setting. The systematic extinctions  $-h + k + l = 3n$  and the Laue symmetry  $\bar{3}m$  were consistent with the rhombohedral space groups  $R\bar{3}m$ ,  $R32$ , and  $R3m$ . The structure was solved and eventually refined in the space group with the highest symmetry,  $R\bar{3}m$ . The data collection was performed on a SIEMENS SMART system with a two-dimensional CCD detector and routine parameters as presented in Table 1.

The structure was solved by direct methods using the SHELXTL PLUS program package, and refined on  $F^2$  with the program SHELXL93 (5). The calculated structure factors were corrected for an isotropic secondary extinction.

During the refinement process unusually high temperature factors, indicating partial occupancies, were observed for Cu(1) on Wyckoff position 6c and for P(3) on position 3a. In order to check for deviations from the nominal compositions, occupancy parameters were refined. For Cu(1) and P(3), a considerable deviation from the full occupancy was found. The occupancy factors of all the other atoms were all within four standard deviations at their ideal values. Therefore, in the final least-squares cycles, only the occupancies of Cu(1) and P(3) atoms were set free. Refinements lead to physically reasonable temperature parameters and an improvement of the  $R$ -factor from 0.055 to 0.045. The empirical formula Ho<sub>2</sub>Cu<sub>6-x</sub>P<sub>5-y</sub> ( $x = 0.41(1)$  and  $y = 0.50(1)$ ) is based on the results of these refinements.

**TABLE 1**  
Crystal Data and Structure Refinement for Ho<sub>2</sub>Cu<sub>6-x</sub>P<sub>5-y</sub>

Empirical formula	Ho <sub>2</sub> Cu <sub>6-x</sub> P <sub>5-y</sub> ( $x = 0.41, y = 0.50$ )
Space group (Pearson symbol)	$R\bar{3}m$ ( $hR13$ )
Unit cell dimensions ( $\text{\AA}$ )	$a = 3.976(1), c = 40.554(8)$
Volume ( $\text{\AA}^3$ )	555.2(4)
Formula units per hexagonal cell	3
Density calcd ( $\text{g cm}^{-3}$ )	7.397
Crystal size ( $\text{mm}^3$ )	$0.18 \times 0.09 \times 0.09$
Diffractometer, rad., monochromator	Siemens SMART, MoK $\alpha$ , graphite
$2\theta$ range for data collection	$4-60^\circ$
Range in $hkl$	$-5 \leq h \leq 5, -5 \leq k \leq 5,$ $-55 \leq l \leq 31$
Number of reflections collected	7579
Independent reflections, $R_{\text{int}}^a$	247, $R_{\text{int}} = 0.0499$
Reflections with $F > 4\sigma(F)$ , $R\sigma^a$	243, $R\sigma = 0.0371$
Data/parameters ( $F > 4\sigma(F)$ )	243/24
Final $R$ ( $R_w$ ) with $F > 4\sigma(F)^a$	0.0453 (0.1273)
$R$ ( $R_w$ ) indices (all data) <sup>a</sup>	0.0455 (0.1273)
Goodness-of-fit (GoF) <sup>a</sup>	1.162

$$^a R_{\text{int}} = \sum |F_o^2 - F_o^2 \text{mean}| / \sum F_o^2.$$

$$R\sigma = \sum \sigma F_o^2 / \sum F_o^2.$$

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$R_w = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}, w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP).$$

GoF =  $(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ , with  $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ ,  $n$  is the number of observed reflections,  $p$  is the number of parameters refined.

Resulting atomic and thermal parameters amplitudes for Ho<sub>2</sub>Cu<sub>6-x</sub>P<sub>5-y</sub> are given in Table 2 and important interatomic distances are compiled in Table 3.

## DISCUSSION

The  $XY$  projections of the Ho<sub>2</sub>Cu<sub>6-x</sub>P<sub>5-y</sub> structure and the atoms' coordination polyhedra (CP) are given in Fig. 1 (see also Fig. 3a). The CP of the Ho atoms is a hexagonal prism, formed from six P (three P1 and three P2) and six Cu

**TABLE 2**  
Atomic Parameters and Anisotropic Temperature Amplitudes for Ho<sub>2</sub>Cu<sub>6-x</sub>P<sub>5-y</sub> ( $x = 0.41, y = 0.50$ )

Atom	Wyckoff			$U_{11}, \text{\AA}^2$	$U_{33}, \text{\AA}^2$	$U_{\text{eq}}, \text{\AA}^2$
	symbol	$x$	$y$			
Ho	6c	0	0	0.07601(2)	0.0170(5)	0.0166(7)
Cu(1) <sup>a</sup>	6c	0	0	0.15667(14)	0.066(3)	0.028(3)
Cu(2)	6c	0	0	0.31135(8)	0.0228(11)	0.0232(15)
Cu(3)	6c	0	0	0.46261(9)	0.0253(11)	0.0298(19)
P(1)	6c	0	0	0.21304(16)	0.0175(16)	0.020(3)
P(2)	6c	0	0	0.37162(15)	0.0164(16)	0.014(3)
P(3) <sup>b</sup>	3a	0	0	0.033(9)	0.042(14)	0.036(8)

Note.  $U_{11} = U_{22}, U_{13} = U_{23} = 0, U_{12} = 1/2U_{11}$ .

<sup>a</sup> Position is occupied by Cu(1) for 79(2)%.

<sup>b</sup> Position is occupied by P(3) for 50(6)%.

**TABLE 3**  
**Interatomic Distances in the Structure  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$**   
**( $x = 0.41, y = 0.50$ )**

Atom	Atom	Distance, Å	Atom	Atom	Distance, Å
Ho-	3 P(2)	2.759(3)	Cu(3)-	3 P(1)	2.324(1)
	3 P(1)	2.915(4)		3 Cu(1)	2.550(3)
	1 P(3)	3.082(1)		3 Cu(1)	2.994(4)
	3 Cu(3)	3.152(3)		1 Cu(3)	3.033(7)
	3 Cu(2)	3.173(3)		3 Ho	3.152(3)
	1 Cu(1)	3.271(6)			
	6 Ho	3.796(1)	P(1)-	1 Cu(1)	2.286(8)
Cu(1)-	1 P(1)	2.286(8)		3 Cu(3)	2.324(1)
	3 Cu(1)	2.435(4)		3 Cu(1)	2.729(5)
	3 Cu(3)	2.550(3)	3 Ho	2.915(4)	
	3 P(1)	2.729(5)	P(2)-	3 Cu(2)	2.389(3)
	3 Cu(3)	2.994(4)		1 Cu(2)	2.444(7)
	1 Ho	3.271(6)		3 Ho	2.759(3)
Cu(2)-	3 P(2)	2.389(2)	3 P(3)	2.771(3)	
	1 P(2)	2.444(7)	P(3)-	6 Cu(2)	2.463(1)
	3 P(3)	2.463(1)		6 P(2)	2.771(3)
	3 Cu(2)	2.906(4)		2 Ho	3.082(1)
		3 Ho	3.173(3)		

(three Cu2 and three Cu3) atoms with all the faces being capped by six Ho, one P3, and one Cu1. The crystallographically different copper atoms have different surroundings. The coordination sphere of the Cu1 atoms is made up from three P1 and three Cu1 in the form of a trigonal prism, from six Cu3 forming another longer trigonal prism rotated by 60° to the first one, and from one P1 and one Ho atoms in front of prismatic bases. The coordination number (*CN*) of Cu2 is 13 (three P2 and three Cu2 making a prism, three P3 and three Ho forming a second prism, plus one P2) and Cu3 atoms have 13 neighbors as well (two trigonal prisms from three P1 and three Cu1, three Cu1, and three Ho, plus one Cu3). P1 and P2 occupy trigonal prisms, made from Ho and Cu or Ho and P atoms, with four additional Cu atoms in front of all the faces and one of the bases and their *CNs* are 10. The P3 atoms are surrounded by 12 atoms (six Cu2 and six P2) in the form of a hexagonal prism and by two Ho atoms capping each base of the prism (the *CN* is 14). Such a large *CN* for P atoms is not very common for rare-earth phosphides and it has been observed only in the  $\text{RE}_3\text{Cu}_{8-y}\text{P}_8$  compounds (4).

The  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  structure is closely related to the  $\text{YbCu}_{3-x}\text{P}_2$  structure (1), but it has additional P atoms on the position 3*a* which remains unoccupied in  $\text{YbCu}_{3-x}\text{P}_2$ . So, the  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  structure is an intercalation version of the  $\text{YbCu}_{3-x}\text{P}_2$  structure and the same relationship was found earlier for  $\text{YbCu}_{2-x}\text{P}_2$  and  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$ , with the latter containing an additional P site. While in  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  the phosphorus site 3*a* is half (50(6)%)

occupied, the additional P site is fully occupied in  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$ . Both  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  and  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  have a similar deficiency for the same copper site in the  $\text{Cu}_4\text{P}_2$  slab (79(2)% in the holmium phosphide and 82(4)% in the yttrium phosphide).

Interatomic distances ( $\delta$ ) in  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  are, in general, close to the sums of the atomic radii; somewhat smaller distances are observed only between P1 and Cu1, Cu3. It may be worth mentioning the P2–P3 distances ( $\delta_{\text{P2-P3}} = 2.771$  Å), although they are larger than the covalent diameter of the P atoms (2.20 Å), there is some interaction and a bonding between these phosphorus atoms.

In the description of the  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  structure (4) special emphasis was given to the structure components, as a crystal chemical approach to the classification of ternary and quaternary phases relies on the decomposition of complex structures into simple elementary components (6). This makes it possible to understand and unify the structural chemistry of known compounds and to estimate their elementary physical properties. In addition, crystal chemical concepts are valuable tools for the prediction of other still undiscovered materials. In (4) the structures of  $\text{YbCu}_{3-x}\text{P}_2$  (1) and  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  have been considered as a linear combination of the close-packed *RE* layers and fragments I and II of the  $\text{Cu}_3\text{P}$  structure (Fig. 2). Stacking of the close-packed *RE* layers with fragments II of  $\text{Cu}_3\text{P}$  gives the structure  $\text{Ce}_2\text{O}_2\text{S}$  (7) that can be found among many phosphides (2) (e.g.,  $\text{PrLi}_2\text{P}_2$  (8)). If the empty prism [ $\text{Cu}_6\text{P}_6$ ] in the fragment II is filled with additional metal atoms, the structure  $\text{LaLi}_3\text{P}_2$  (9) will be produced. A fragment II with intercalated atoms is designated II\* (Fig. 2).

The structure  $\text{YbCu}_{3-x}\text{P}_2$  (1) is formed from fragments I and II of  $\text{Cu}_3\text{P}$  interspaced with the Yb layers. If fragments II are substituted for II\* ones, while the stacking order of building blocks I and II and the *RE* layers is kept the same, the  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  structure will be obtained. So, like  $\text{YbCu}_{2-x}\text{P}_2$  and  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  the two structures  $\text{YbCu}_{3-x}\text{P}_2$  and  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  can be viewed as a linear combination of the fragments (I and II or II\*) of  $\text{Cu}_3\text{P}$  and *RE* layers. If blocks I of the  $\text{Cu}_3\text{P}$  are interspaced only with *RE* (or Ca) layers, another structure ( $\text{CaCu}_4\text{P}_2$  type) can be formed with some representatives among rare-earth copper phosphides ( $\text{RECu}_{4-x}\text{P}_2$  (10)).

Through the paper the defects on the Cu and P sites in the structure are intentionally presented by *x* and *y* in order to make its description easier and to present the structural relationship more clearly. In the case of  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  three fragments I ( $\text{Cu}_4\text{P}_2$ ) and three fragments II\* ( $\text{Cu}_2\text{P}_3$ ) are stacked in a changing order to form the hexagonal unit cell of the holmium phosphide, and, taking into account that they are sharing the Ho atoms, the contents of the cell without the defects can be presented by the formula  $(\text{HoCu}_2\text{P}_3)_3(\text{HoCu}_4\text{P}_2)_3$  or  $\text{Ho}_{3+3}(\text{Cu}_2\text{P}_3)_3(\text{Cu}_4\text{P}_2)_3$ . A rhombohedral unit cell, which is one-third the size of

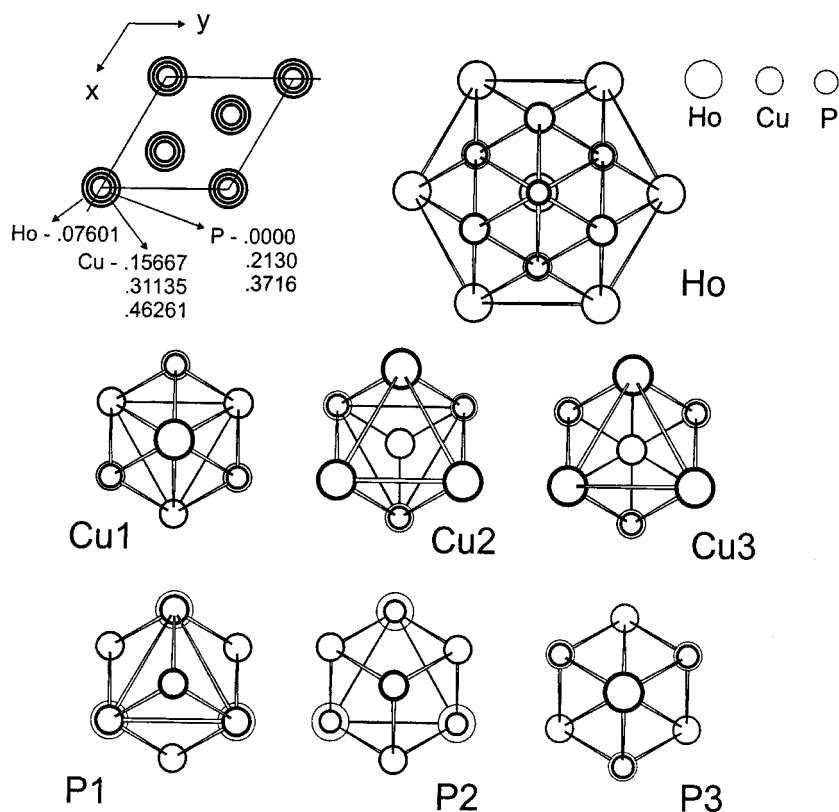


FIG. 1.  $XY$  projection of the  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  structure and coordination polyhedra of the atoms.

a hexagonal one, is described with the  $\text{Ho}_{1+1}(\text{Cu}_2\text{P}_3)$  ( $\text{Cu}_4\text{P}_2$ ) or  $\text{Ho}_2\text{Cu}_6\text{P}_5$  formula. Since it can be assumed that the number of each block per unit cell could be different and there are no restrictions concerning their stacking order, the general composition of this series of compounds can be written as  $RE_{m+n}(\text{Cu}_2\text{P}_3)_m(\text{Cu}_4\text{P}_2)_n$ . In the holmium phosphide  $m$  and  $n$  take the value of unity but they may have also other values. If  $m = 2$  and  $n = 1$ , we obtained the second number of the series  $RE_{2+1}(\text{Cu}_2\text{P}_3)_2(\text{Cu}_4\text{P}_2)$  or  $RE_3\text{Cu}_8\text{P}_8$  and this case is practically realized with yttrium and other heavy rare earths (4) to produce the  $\text{Y}_3\text{Cu}_{8-x}\text{P}_8$  structure. Since the number of  $\text{Cu}_2\text{P}_3$  building blocks (fragments II\*) is double that of  $\text{Cu}_4\text{P}_2$  (fragments I), the alternate stacking, as observed in  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  (see Fig. 3), is not possible and two layers of the same type are joined together. Knowing the thickness of individual layers (6.165 Å and 7.353 Å in the case of  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$ ), a  $c$  parameter of a unit cell may be calculated for given values of  $m$  and  $n$ . The experimentally obtained  $c$  parameter for  $\text{Y}_3\text{Cu}_{8-x}\text{P}_8$  is 60.14(1) Å (4), in reasonable agreement with the calculated value of 59.049 Å, based on the data of the  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  layers. On the other hand, knowing the  $c$  parameter from the experiments and assuming the layers

are similar in thickness, the values of  $m$  and  $n$  can be determined.

The  $RE\text{Cu}_{4-x}\text{P}_2$  phosphides (10) can also be approached in the same way, but now the  $\text{Cu}_2\text{P}_3$  building blocks (fragment II\*) are missing and the unit cell must be formed only from the  $\text{Cu}_4\text{P}_2$  ones (fragment I). For the rhombohedral unit cell we need three such blocks to get the periodicity in the  $c$  direction, so the compounds can be represented with the formula  $RE_{0+3}(\text{Cu}_2\text{P}_3)_0(\text{Cu}_4\text{P}_2)_3 = RE_3(\text{Cu}_4\text{P}_2)_3$  in the hexagonal setting and with  $RE\text{Cu}_4\text{P}_2$  for the rhombohedral unit. This gives  $m = 0$  and  $n = 1$  for the general formula  $RE_{m+n}(\text{Cu}_2\text{P}_3)_m(\text{Cu}_4\text{P}_2)_n$ . We can estimate the  $c$  parameter for  $RE\text{Cu}_{4-x}\text{P}_2$  in the same way we did for  $\text{Y}_3\text{Cu}_{8-x}\text{P}_8$ , using the thickness of the  $\text{Cu}_4\text{P}_2$  slab from  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$ :  $3 \times 7.353 = 22.059$  Å, which is in really good correspondence with (10) ( $c = 22.734$  Å for  $\text{EuCu}_{3.8}\text{P}_2$ , 21.748 Å for  $\text{HoCu}_{3.7}\text{P}_2$ , etc.), even without making allowance for Cu deficiencies, rare-earth's radii, some other electronic factors, and preparation methods.

Finally we would like to address the question of the partial occupancy (50%) of P3. The electron density of P3 corresponds to the electron density of oxygen. But the analysis of the interatomic distances and coordination

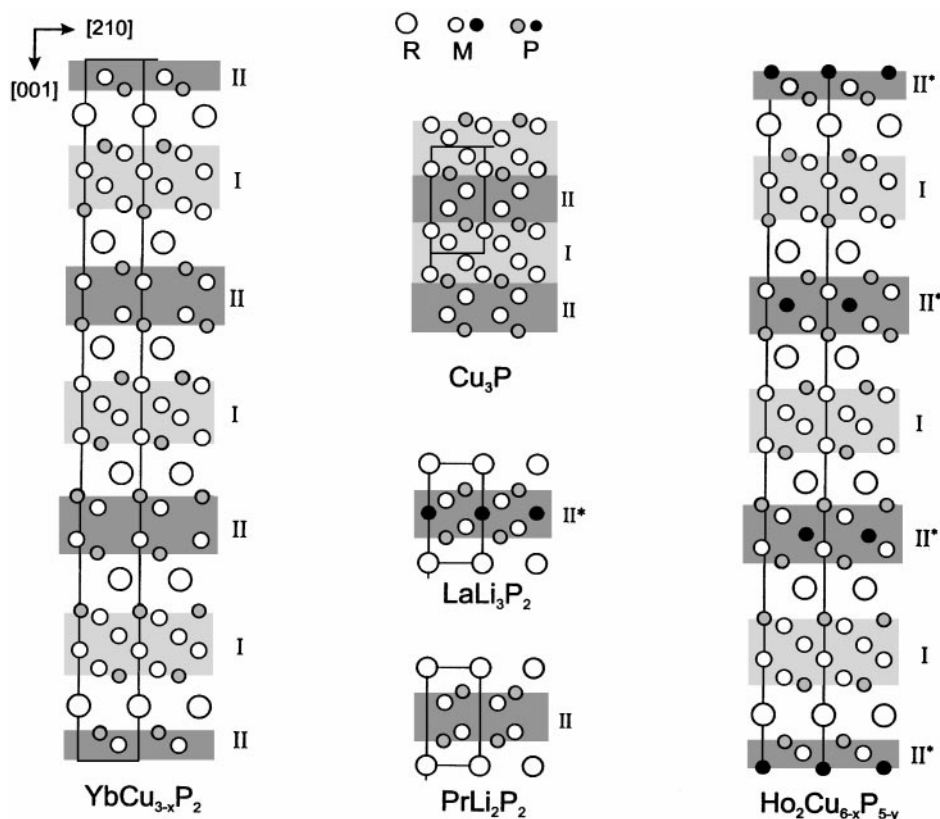


FIG. 2. Structures of  $\text{YbCu}_{3-x}\text{P}_2$  and  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  as a stacking of the fragments of  $\text{Cu}_3\text{P}$  (light gray section I and dark gray section II or II\*) and layers of a rare-earth close packing. Solid black circles are additional atoms intercalated in the voids of the  $\text{Cu}_3\text{P}$  structure.

spheres indicates that this position is unlikely to be occupied by oxygen atoms. If oxygen is assumed instead of phosphorus, rather short distances can be expected between oxygen atoms and close neighbors, which are Cu atoms in our case. The Cu–O distances in  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  are 1.68 Å (11) and 1.826 Å (12), respectively; in  $\text{Cu}_4\text{O}_3$  distances vary from 1.872 to 1.972 Å (13). In these oxides the O atoms have two close neighbors. In ternary and quaternary phases Cu–O distances are close to or a little larger than those in the copper oxides. In  $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_3$  and  $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$  ( $x = 0.0$ – $1.0$ ) the Cu–O distances vary from 1.93(4) to 2.00(6) Å (14). Also, the Cu–O distances in phosphates, e.g.,  $\text{Sr}_3\text{Cu}_3(\text{PO}_4)_4$ ,  $\text{Pb}_3\text{Cu}_3(\text{PO}_4)_4$ ,  $\text{BaCu}_2(\text{PO}_4)_2\text{H}_2\text{O}$ , and  $\text{Ba}_2\text{Cu}(\text{PO}_4)_2\text{H}_2\text{O}$ , are rather short (1.940 to 2.199 Å), although oxygen atoms are considered to be primarily and closely bound (1.499 to 1.586 Å) to phosphorus atoms in the  $\text{PO}_4^{3-}$  units (15). In these compounds O atoms have two neighbors at relatively short separation, with others atoms being at larger distances. In  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  ( $x = 0.41$ ,  $y = 0.50$ ) the O atoms would have six Cu atoms at 2.463(1) Å, which would be very unusual.

We can also assume interstitial water molecules instead of P3, but similarly to oxygen in the previous compounds water oxygen atoms usually have two close neighbors, not six.

In compounds  $\text{Ln}_{3-x}\text{Cu}_{8-y}\text{P}_8$  there is the same phosphorus site in the  $\text{Cu}_2\text{P}_3$  units (fragment II\*) and this position is now fully occupied (4). The structural relationship discussed in this paper shows how the structures  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  ( $\text{Ln}_{3-x}\text{Cu}_{8-y}\text{P}_8$  compounds) and  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  can be built from the  $\text{Cu}_4\text{P}_2$  and  $\text{Cu}_2\text{P}_3$  blocks. It is unlikely for a  $\text{Cu}_2\text{P}_3$  unit to have phosphorus atoms in  $\text{Ln}_{3-x}\text{Cu}_{8-y}\text{P}_8$  and oxygen atoms in  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$ .

The interatomic distance Cu–P3 of 2.463(1) Å is characteristic of Cu–P bonds, although this interaction is a little larger than some Cu–P bonds. The larger coordination sphere of P3 accounts for this increase. In  $\text{LiCu}_2\text{P}_2$  the Cu–P distance is 2.35 Å (16), but in  $\text{GdCu}_{4-x}\text{P}_2$  the Cu–P distances are 2.252, 2.564, and 3.002 Å (10).

Why these phosphorus sites are empty in the compounds  $\text{YbCu}_{3-x}\text{P}_2$  and  $\text{YbCu}_{2-x}\text{P}_2$  (1), which have structures similar to those of  $\text{Y}_3\text{Cu}_{8-y}\text{P}_8$  and  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$ , is an interesting question.

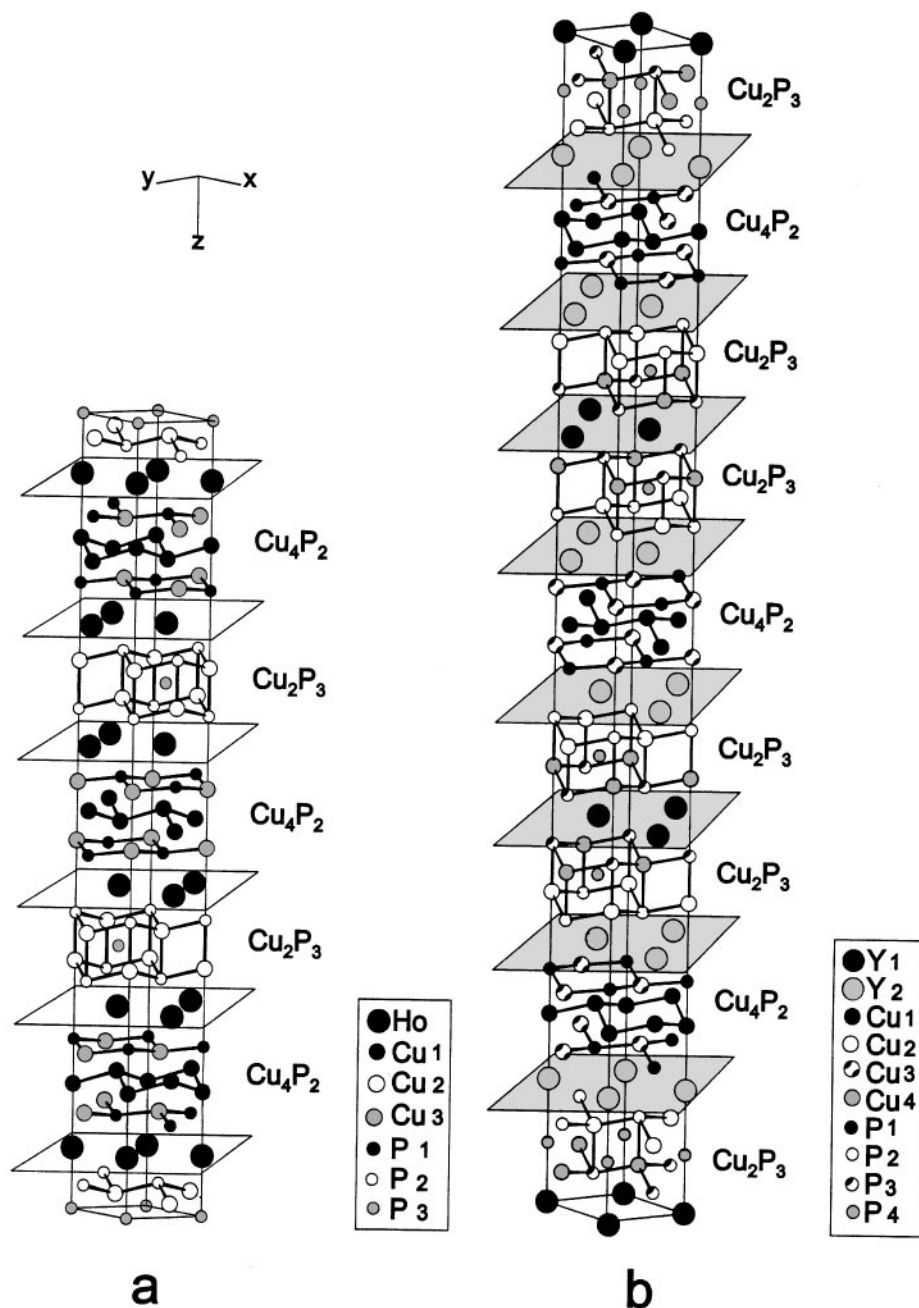


FIG. 3. Crystal structures of  $\text{Ho}_2\text{Cu}_{6-x}\text{P}_{5-y}$  (a) and  $\text{Y}_3\text{Cu}_{8-x}\text{P}_8$  (b) as a stacking of  $\text{Cu}_2\text{P}_3$  and  $\text{Cu}_4\text{P}_2$  units.

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#### REFERENCES

1. P. Klüfers, A. Mewis, and H. U. Schuster, *Z. Kristallogr.* **149**, 211 (1979).
2. Yu. Kuz'ma and S. Chykhrij, in "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gscheidner, Jr., and L. R. Eyring, Eds.), Vol. 23, p. 285, Elsevier, Amsterdam, 1996.
3. Yu. B. Kuz'ma, Yu. A. Mozharivskiy, and O. N. Panas, *Inorg. Mater.* **34**, 7 (1998).
4. Yu. B. Kuz'ma, S. I. Chykhrij, Yu. A. Mozharivskiy, W. Tremel, and R. O. Demchyna, *J. Alloys Compd.* **278**, 169 (1998).
5. G. M. Sheldrick, SHELX93, Program for Crystal Structure Refinement, Universität Göttingen, 1993.
6. E. Parthé and B. Chabot, "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gscheidner, Jr. and L. R. Eyring, Eds.), Vol. 6, p. 113, Elsevier, Amsterdam, 1983.

7. W. H. Zachariasen, *Acta Crystallogr.* **2**, 60 (1949).
8. H. O. Fischer and H. U. Schuster, *Z. Naturforsch. b* **35**, 1322 (1980).
9. I. Grund, H. U. Schuster, and P. Müller, *Z. Anorg. Allg. Chem.* **515**, 151 (1984).
10. J. Dünner and A. Mewis, *Z. Anorg. Allg. Chem.* **623**, 608 (1997).
11. G. Tunel, E. Posnjak, and C. J. Ksanda, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem. A* **90**, 120 (1935).
12. Z. G. Pinsker and R. M. Imanov, *Sov. Phys.-Crystallogr.* **9** (3), 334 (1964) (Translated from *Kristallografiia*).
13. M. O'Keffe and J.-O. Bovin, *Am. Mineral.* **63**, 180 (1978).
14. P. Porta, S. De Rossi, M. Faticanti, G. Mineli, I. Pettiti, L. Lisi, and M. Turco, *J. Solid State Chem.* **146**, 291 (1999).
15. H. Effenberger, *J. Solid State Chem.* **142**, 6 (1999).
16. H. von Schlenger, H. Jacobs, and R. Juza, *Z. Anorg. Allg. Chem.* **385**, 177 (1971).